Research Article

Kinetics of Thermolysis of Nickel(II) Perchlorate Complex with n-Propylamine

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Received 25 November 2013; Accepted 10 January 2014; Published 19 February 2014

Academic Editors: J. Luo and H. S. Yathirajan

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Complex of nickel perchlorate with n-propylamine has been synthesised with molecular formula $[\text{Ni}(\text{n-pa})_3(\text{ClO}_4)(\text{H}_2\text{O})]\text{ClO}_4$. It has been characterised by elemental analysis, thermogravimetry, UV-VIS, and IR spectroscopic data. Thermal properties have been investigated by thermogravimetry (TG) in static air and by simultaneous thermogravimetry-derivative thermogravimetry-differential thermal analysis (TG-DTG-DTA) in flowing nitrogen atmosphere. Kinetics of thermolysis has been analysed applying model-fitting and model-free isoconversional method on isothermal TG data recorded at five different temperatures. To observe the response of complex towards fast heating, explosion delay time has been recorded at various temperatures and kinetics of explosion has been studied using these data.

1. Introduction

Metal perchlorates have strong oxidizing properties and amines are reducing in nature. Amines have strong e^- donation power due to presence of lone pair e^- on their nitrogen atom. These two oxidizing and reducing groups can be easily incorporated in a single molecule by reacting metal perchlorate with amine resulting in the formation of metal amine perchlorate coordination compounds. Any composition having strong oxidizing and reducing groups simultaneously in a molecule will exhibit the properties of high energetic materials. Thus, metal perchlorate amine complexes will exhibit the properties of energetic material and undergo autotransmitted decomposition reactions [1–3] when subjected to a stimuli (heat, friction, shock, wave, etc.). Owing to their energetic properties these types of complexes have found applications in explosives, pyrotechnics, and propellants. Such type of complexes has been proved to be a strong burning rate modifier for hydroxyl terminated polybutadiene-ammonium perchlorate (HTPB-AP) based propellants [4, 5]. In search of insensitive high energetic materials, a strong interest is being given by the researches on such type of complexes (having oxidizing and reducing

group in one molecule) and they have been synthesized and their properties have been extensively investigated [5–14]. In the present paper, we report the preparation, characterisation, thermolysis, and explosion characterisation of nickel perchlorate complex with n-propyl amine, water, and ClO_4^- as ligands. Kinetics of early thermolysis was also investigated by applying model-fitting and isoconversional method.

2. Experimental

2.1. Materials. Nickel carbonate, perchloric acid, n-propyl amine (sd.fine), ethanol (Changshu Yangyuan Chemical, China), petroleum ether (Merk), and all of AR grades were used as received.

2.2. Preparation. The complex was prepared via two-step procedure. In first step hexahydrate nickel perchlorate was obtained by reacting nickel carbonate with 60% perchloric acid followed by recrystallisation. In second step, ethanolic solution of nickel perchlorate and n-propyl amine was mixed together, stirred well at room temperature, and filtered out some obtained light green ppt. From the filtrate, after 2–3 days

TABLE 1: IR frequencies and elemental analysis data for the complex.

ν (cm ⁻¹)	IR Assignments	Element %	observed/calculated
448	M-N	C	22.4/22.1
627	Ionic perchlorate	N	8.6/8.5
753	C-H def	H	6.1/6.4
990	C-N str.	Ni	12.95/13.27
1089	Ionic perchlorate		
1112	Bidentate		
1145	ClO ₄ ⁻		
1395	C-NH ₂		
1503	N-H bend.		
1570			
2705	C-H str.		
2994			
3034	NH ₂ (Pri)		
3434	O-H (H ₂ O)		

FIGURE 1: TG curve of complex in static air atmosphere.

light green crystals of desired complex were obtained. The crystals were washed with alcohol and dried.

Caution. Perchlorates are explosives. They should be handled with care. However, I have not found any problem during all experimental procedures.

2.3. Characterisation. Characterisation of complex was done by elemental analysis (C, H, N; Thermo Finnigan Flash EA 1112 CHNS analyzer), infrared [15–17] (Perkin Elmer FT-IR spectrometer), UV-VIS spectroscopy and thermogravimetry (Table 1).

2.4. Thermal Analysis

2.4.1. TG in Air. Thermogravimetry in static air with heating rate of 10°C/min (Figure 1) was recorded using an indigenously fabricated TG apparatus [18] (sample mass 20 mg).

FIGURE 2: TG-DTG-DTA curve of complex in flowing nitrogen atmosphere.

2.4.2. Simultaneous TG-DTG-DTA. These traces were obtained in flowing nitrogen atmosphere (100 mL/min), sample was ~2.5 mg at a heating rate of 10°C/min (Figure 2, Table 2).

2.4.3. Isothermal TG. Isothermal TG (Figure 3) was recorded in static air atmosphere using the same indigenously fabricated TG apparatus as mentioned earlier at five different temperatures (200, 210, 220, 230, and 240°C). Sample mass taken was 10 mg and readings were recorded for 30% decomposition.

2.4.4. Kinetic Analysis. Kinetics of decomposition has been investigated using isothermal TG data using model fitting (Table 3) [19] and isoconversional method [20, 21]. Variation of activation energy with extent of conversion α is shown in Figure 4.

2.4.5. Explosion Delay Experiments. This experiment was performed using tube furnace technique [22] (sample mass 10 mg) at temperatures of 280, 300, 320, 340, and 360°C within experimental limit of $\pm 1^\circ\text{C}$ (Table 4). D_E data were fitted in Arrhenius equation

$$D_E = A \exp \frac{E^*}{RT}, \quad (1)$$

where A is the Arrhenius factor, E^* is the activation energy for explosion, T is absolute temperature, and R is the gas constant. A plot of $\ln D_E$ versus $1/T$ is presented in Figure 5.

3. Results and Discussion

Table 1 containing elemental analysis and IR data shows a good agreement between observed and calculated percentages of C, H, N, and Ni. The FT-IR spectra of the complex revealed bands at 448 cm⁻¹ assigned to $\nu(\text{M-N})$, 627 and 1089 cm⁻¹ assigned to ionic perchlorate, and 1112 and 1145 cm⁻¹ assigned to bidentate perchlorate ion (C_{2v} symmetry) [22]. A broad peak at 3434 cm⁻¹ is due to $\nu(\text{O-H})$ of coordinated water. Other peaks are according to standard text. In the UV-VIS spectrum, the absorption maxima at 263 nm is due to $n \rightarrow \pi^*$ transition and a peak at 378 nm is assigned for $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P})$ overlapping with charge

TABLE 2: TG-DTA data of the complex.

Step	TG		DTA	
	Temperature range (°C)	% decomposition	Peak position (°C)	Nature of peaks
I	92–121	4	169	Endo
II	121–288	12	—	—
III	290–305	70	299	Exo

TABLE 3: Activation energy (E), Arrhenius factor, and correlation coefficients (r) for the isothermal decomposition of the complex.

Serial number	Model	$\ln A$	Slope	$E/\text{kJ mole}^{-1}$	r	Mean deviation	Standard deviation
1	Power law ^{3/4}	1.1382	2128.2	17.7	0.9702	2.728	2.877
2	Power law ^{2/3}	1.2143	1978.1	16.4	0.9641	2.613	2.756
3	Power law ^{1/2}	0.6130	2148.7	17.8	0.9714	2.486	2.628
4	Power law ^{-1/2}	0.0605	2207.1	18.3	0.9740	2.269	2.384
5	Power law ⁻¹	-0.0051	2224.6	18.5	0.9742	2.254	2.378
6	Mampel ($1 - \alpha$)	-1.1053	2275.1	18.9	0.9610	1.755	1.853
7	$a \cdot e^{3/4}$	0.7241	2177.1	18.1	0.9748	2.570	2.711
8	$a \cdot e^{2/3}$	-0.0275	2249.8	18.7	0.9599	2.268	2.390
9	$a \cdot e^{1/2}$	-0.4144	2260.2	18.8	0.9605	2.085	2.201
10	cs	0.2240	2249.1	18.7	0.9686	2.393	2.525
11	T-d-diff	0.2629	2305.1	19.1	0.9614	2.470	2.605
12	cc	0.1869	2223.4	18.5	0.9713	2.349	2.478
13	P-T	-1.6300	2237.5	18.6	0.9592	1.454	1.536
14	G-B	1.2040	2256.1	18.7	0.9698	2.891	3.049

FIGURE 3: Isothermal TG of complex in static air atmosphere at different temperatures.

FIGURE 4: Variation of activation energy of thermolysis for the complex with extent of conversion (α).

transfer band. A band at 870 nm is assigned for $^3A_{2g}(F) \rightarrow ^1E_g(D)$ transition. Thus, as suggested by the overall evidence given above, the complex can be formulated as $[\text{Ni}(\text{n-pa})_3(\text{ClO}_4)(\text{H}_2\text{O})]\text{ClO}_4$ in which Ni^{2+} is hexacoordinated. Out of six coordination sites, three sites are satisfied with nitrogen atoms; one from each n-propylamine and three sites with O-atoms; one from water molecule and two from one of the perchlorate ions acting as a bidentate ligand (C_{2v} symmetry).

A perusal of TG curve recorded in static air with linear temperature increase shows that the complex decomposes in three steps. The very first step (92–121°C) is gradual in which

coordinated H_2O leaves the complex (~4% wt. Loss). In the second step (121–288°C) one of the n-propylamines is released (~12% wt. Loss). In the third step (290–305°C) the remaining residue $[\text{Ni}(\text{n-pa})_2(\text{ClO}_4)]\text{ClO}_4$ (might be tetracoordinated complex of Ni^{2+}) ignites with smoke and low noise giving a sharp weight loss (~70%). At lost ~15% mass is left which corresponds to NiO (calculated mass 15.27%). In flowing N_2 atmosphere (Figure 2) the decomposition pattern of complex is similar to static air. A DTG peak has been obtained corresponding to third step sudden weight loss. DTG were not obtained for first step because this step is very gradual. DTG peak for second step might be incorporated in third step

TABLE 4: Explosion delay, activation energy for thermal explosion (E^*), and correlation coefficient (r) of complex.

$D_E D_E$ (s) at temperature ($^{\circ}\text{C}$)					E^* (kJ mol^{-1})	r	$\ln k$
280 $\pm$ 1	300 $\pm$ 1	320 $\pm$ 1	340 $\pm$ 1	360 $\pm$ 1			
123	93	83	58	54	30.9	0.9842	-1.915

FIGURE 5: Graph representing $\ln D_E$ versus $1/T$ for the complex.

of DTG peak. In DTA curve an endotherm at 169°C and this is to be in harmony with second step (removal of one of the n-pa molecule). A strong exothermic peak at 299°C has been received which suits the ignition of partially decomposed residue in the third step.

Thus, in the light of the above discussion, the thermolysis pattern of the complex can be given as

In the order to calculate activation energy (E_a) for the removal of ligands (30% wt. Loss which includes H_2O and 2 n-pa molecule), a set of reaction models (Table 3) [19] was used on isothermal TG data in the temperature range $200-240^{\circ}\text{C}$ (Figure 3). E_a values obtained ($\sim 18 \text{ kJ mole}^{-1}$) are almost equal irrespective of the reaction model used.

Kinetic analysis of isothermal TG data applying isoconversional method [20, 21] concerns with the calculation of activation energy independent of the model but corresponding to the extent of conversion (α) of the complex. Figure 4 shows that at different values of α , E_a values in are different. Model-free isoconversional method is a better approach to obtain reliable and consistent kinetic data as compared to model-fitting methods.

The complex when subjected to sudden high temperature explodes with noise. To determine the activation energy of explosion (E^*) explosion delay time has been recorded at five different temperatures (Table 4). Activation energy for explosion was found to be 30.9 kJ mol^{-1} . A graph of $\ln D_E$ versus $1/T$ (Figure 5) shows that explosion delay time exponentially depends on temperatures.

4. Conclusion

The complex has been prepared and characterised by various techniques. TG-DTA study reveals that the complex decompose in three steps. After an initial weight loss ($\sim 16\%$) oxidiser (ClO_4^-) and fuel (reducing group i.e., n-pa) lead to ignition giving a sharp exothermic peak in DTA. End product of thermolysis corresponds to NiO. Complex explodes when kept suddenly under high temperatures.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors thank the Secretary Board of Management, Principal and Head of Department of Chemistry, DBS College, Kanpur, for providing laboratory facilities, and University Grants Commission, New Delhi, for financial assistance. Thanks are also due to Sophisticated Test and Instrumentation Centre, Cochin University of Science and Technology, for CHN, FT-IR, UV-VIS, and TG-DTA analyses.

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