Journal of Thermal Analysis, Vol. 32 (1987) 1369–1379

THERMAL DEGRADATION OF SOME COORDINATION POLYMERS

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(Received February 26, 1986)

Coordination polymers of Co(II), Ni(II) and Cu(II) were synthesized using two ligands, 5-benzylidene pseudothiohydantoin and 5-cinnamylidene pseudothiohydantoin. These polymers were characterized by dynamic and static TG, and their relative thermal stabilities were compared. The thermal stabilities found by dynamic and static TG were in harmony. The structure of the polymeric unit for each polymer was predicted with the help of thermoanalytical data. The data reveal one pattern for Co(II) and Cu(II), i.e. an $(ML_2)_n$-type polymerkc unit, and another pattern for Ni(II), i.e. an $(ML_2 \cdot 2H_2O)_n$-type polymeric unit. The static (isothermal) TG data were analysed by use of (i) the difference equation method, and (ii) the Avrami–Erofeyev method. The activation energies of the coordination polymers were calculated, and it was observed that the chelate polymers of Ni(II) with both ligands were more stable than those of Co(II) and Cu(II). This prediction on the basis of static TG data is in agreement with the prediction based on the activation energies and initial decomposition temperatures calculated from the dynamic TG curves.

The ligands 5-benzylidene pseudothiohydantoin (BPTH) and 5-cinnamylidene pseudothiohydantoin (CPTH), derivatives of pseudothiohydantoin (PTH), may be synthesized by known methods [1–3]. PTH contains nitrogen, oxygen and sulphur donor atoms, and when it coordinates to metal ions it may form MO_2N_2 or MS_2N_2 chromophores. Since chelate polymers have a large number of practical applications, it is necessary to investigate the effects of heat on such polymers in order to establish their thermal stabilities.

A wide variety of thermally stable polymers have been synthesized and the sequences of their thermal stabilities have been predicted from their TG data. Chand et al. [4] studied the thermal stabilities of metal ion-bis-(β-diketone) polymers and suggested the sequence of thermal stability to be Be(II) > Cu(II) > Ni(II) > Zn(II) > Co(II). Singh, Maurya and Dey [5] synthesized a series of coordination polymers of metals belonging to the first transition series with terephthalaldehyde bis-(semicarbazone). They proposed that terephthalaldehyde

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bis-(semicarbazone) acts as a tetradentate ligand and coordinates through enolic oxygen and azomethane nitrogen atoms. They predicted the sequence of thermal stability to be Zn > Ni > Co > Mn > Cu.

The kinetic properties of coordination polymers have also been studied. The polycoordination of 4,4′-bis-(acetoacetyl) diphenyl ether with Be(acetylacetonate) [6] was found to proceed by a bimolecular mechanism. Efendieve [7] studied the rates of sorption and desorption, and the rate of leaching of Cu^{2+} ions with polymeric diethyl vinyl phosphinate.

Various methods have been used to analyse the thermoanalytical data. Ozawa [8] suggested a method of analysing the thermoanalytical data for the non-isothermal degradation of calcium oxalate and Nylon-6, and considered the applicability of the method to other types of thermal analysis. He also proposed a method of analysing thermal data by transforming them to equivalent isothermal data and utilizing linear relations to elucidate the mechanism of degradation [9].

In the present communication we report the relative thermal stabilities of some chelate polymers of Co(II), Ni(II) and Cu(II) on the basis of their activation energies, calculated from non-isothermal TG data using the Sharp–Wentworth method [10, 12] as well as from isothermal TG data via (two well-known methods [13–17] widely used in the field of organic polymers. The tentative compositions and structures of the polymeric units have also been proposed. These display good agreement with the results of elemental analysis, electronic spectral, IR spectral and magnetic measurement studies [11].

Experimental

Materials

Chemicals: All chemical used were of Analar grade.

Synthesis of ligands: The ligands 5-cinnamylidene pseudothiohydantoin and 5-benzylidene pseudothiohydantoin were prepared by known methods [1–3].

Synthesis of coordination polymers: An equimolar mixture of ligand and metal acetate was dissolved in the minimum volume of DMF. The resulting mixture was refluxed over a water-bath for 6–8 hours. The insoluble polymers formed were filtered off and washed thoroughly several times with DMF and absolute alcohol to remove unreacted ligand and metal acetate. The polymers thus obtained were vacuum-dried. The metal-chelate polymers were all air-stable, coloured powders, insoluble in water and common organic solvents such as ethanol, acetone, chloroform, benzene, nitrobenzene, etc.

Methods

Thermogravimetry (TG)

(A) *Non-isothermal TG*

The non-isothermal TG measurements were carried out using a thermobalance fabricated at the Central Instrumentation Centre, Nagpur University, Nagpur. A chromel-alumel thermocouple with a temperature range 20° to 700° was used as a temperature indicator. All measurements were made at a linear heating rate of 5 deg $\min^{-1}$ in air. An accurately weighed dried chelate polymer powder (70 mg) in a platinum crucible was hung in the furnace and the mass loss was recorded at regular intervals of 20° until the mass loss was complete. TG curves for each polymer were obtained by plotting the percentage mass loss as a function of temperature.

(B) *Isothermal TG*

Isothermal experiments were recorded in terms of mass loss versus time. The powdered polymer samples (70 mg) were degraded in air at a constant temperature by heating the samples in a platinum crucible. The isothermal weight change determinations were carried out at temperatures where the intermediate products were stable and at the point where decomposition starts. These temperatures were decided from the non-isothermal TG curves.

Results and discussion

Non-isothermal thermogravimetry: A plot of percentage mass loss versus temperature is shown in Fig. 1 for a representative Ni(II)-BPTH chelate polymer. From the TG curves, the thermoanalytical data and the decomposition temperatures were determined as given in Table 1. The tentative compositions of the polymeric units are also given in Table 1. To obtain the relative thermal stabilities of the various chelate polymers, the method described by Sharp and Wentworth [10, 12] was adopted. The activation energies in the different temperature ranges are given in Table 2. The thermal stabilities of the polymers, based on the initial decomposition temperatures, have also been used here to define their relative thermal stabilities, neglecting the degree of decomposition (Table 1).

A close examination of Tables 1 and 2 reveals that there is a definite relationship between the thermal stabilities of the metal-chelate polymers of BPTH and CPTH. The sequence of thermal stability was found to be Ni(II) > Cu(II) > Co(II). The sequence of thermal stability of the polymers predicted on the basis of the initial decomposition temperatures is in harmony with that predicted from the activation

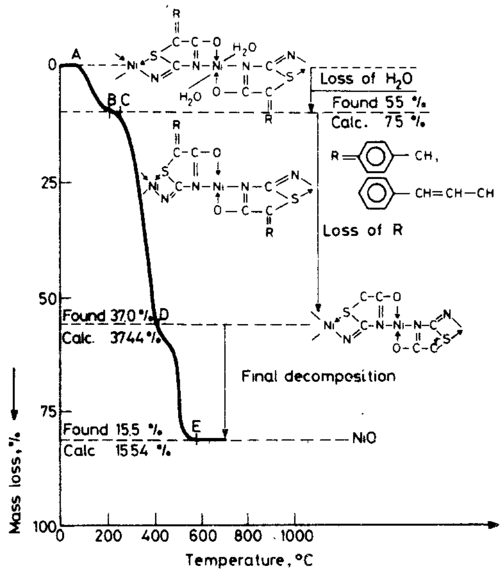


Fig. 1 Decomposition pattern of the representative polymer $[Ni(II)(BPTH)_2 \cdot 2H_2O]_n$

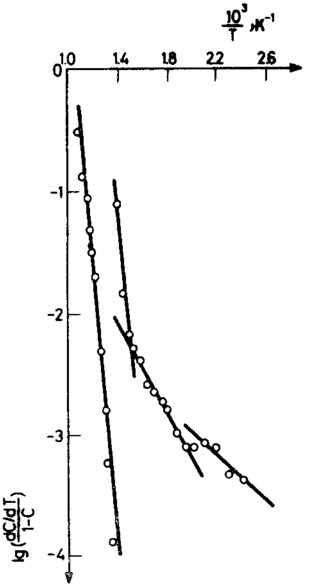
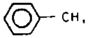
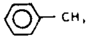
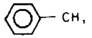
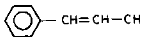
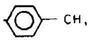
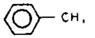


Fig. 2 Sharp–Wentworth plots for the polymer $[Ni(II)(BPTH)_2 \cdot 2H_2O)_n$

Table 1 Thermoanalytical data and decomposition temperatures for various metal-chelate polymers

Tentative composition of polymer	Temperature, °C	% Mass loss		Probable composition after degradation	Free part of ligand	% Mass loss		Decomposition temperature, °C
		found	calcd.			found	calcd.	
1 $[Co(II)(BPTH)_2]_n$	620	77.5	82.66	Co_3O_4	*IN BPTH* 	36.5	38.88	340
2 $[Ni(II)(BPTH)_2 \cdot 2H_2O]_n$	200 640	5.5 84.5	7.5 84.46	$[Ni(II)(BPTH)_2]_n$ NiO		37.0	37.44	380
3 $[Cu(II)(BPTH)_2]_n$	620	70.0	71.31	*Cu_2O		38.5	36.09	300
4 $[Co(II)(CPTH)_2]_n$	580	81.0	84.41	Co_3O_4	*In CPTH* 	48.0	45.05	320
5 $[Ni(II)(CPTH)_2 \cdot 2H_2O]_n$	200 620	9.5 81.5	6.54 86.4	$[Ni(II)(CPTH)_2]_n$ NiO		45.5	42.13	360
6 $[Cu(II)(CPTH)_2]_n$	620	70.5	72.46	*Cu_2O		40.5	44.65	300

* The residue of copper oxide has a composition close to that of Cu_2O. This may be due to the reduction of Cu(II) to Cu(I) in the presence of the sulphur in the ligand.

Table 2 Activation energies of the metal-chelate polymers

No.	Polymer	Temperature range, °C	Energy of activattion, E_a J/mol
1	$[Co(II)(BPTH)_2]_n$	120–180	−27.25
		180–280	16.59
		280–420	70.02
2	$[Ni(II)(BPTH)_2 \cdot 2H_2O]_n$	100–200	18.07
		200–400	36.25
		400–440	190.78
		440–640	381.57
3	$[Cu(II)(BPTH)_2]_n$	100–200	−14.04
		200–260	20.28
		260–460	177.52
4	$[Co(II)(CPTH)_2]_n$	160–220	14.93
		220–280	36.42
		280–360	190.78
		360–560	128.53
5	$[Ni(II)(CPTH)_2 \cdot 2H_2O]_n$	100–200	17.34
		200–320	23.85
		320–440	191.46
		440–640	410.24
6	$[Cu(II)(CPTH)_2]_n$	100–160	15.10
		160–260	19.08
		260–380	83.94
		380–640	275.22

energy values. Except for Co(II--polymers, the thermal degradation of the other polymers involve a major two-step process after the loss of hydration water molecules. The first step of decomposition after the loss of hydration/coordinated water is fast compared to the second step of decomposition. This may be due to the fact that the non-coordinated part of the ligand decomposes first, while the actually coordinated chromophore decomposes later. The proposed composition of the chelate polymers of Co(II) and Cu(II) is $(ML_2)_n$, while those of Ni(II) is $(ML_2 \cdot 2H_2O)_n$. The tentative structure of the polymeric unit in each case is shown in Fig. 7.

Isothermal thermogravimetry: Plots of percentage mass loss versus time are shown in Fig. 3. The rate of mass loss increases as the temperature is raised. The kinetic parameters of degradation were determined for the six chelate polymers using the difference equation method [13–15] and the Avrami–Erofeyev [16, 17] equation. The plots in the difference equation method and the Avrami–Erofeyev method for the representative $[Ni(II)(BPTH)_2 \cdot 2H_2O]_n$ are shown in Figs 4 and 5,

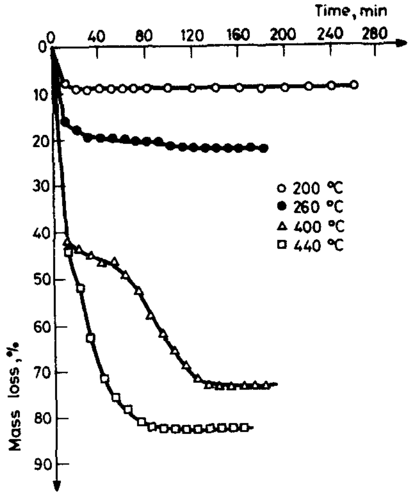


Fig. 3 Mass loss *vs.* time for the thermal decomposition of the polymer $[Ni(II)(BPTH)_2 \cdot 2H_2O]_n$

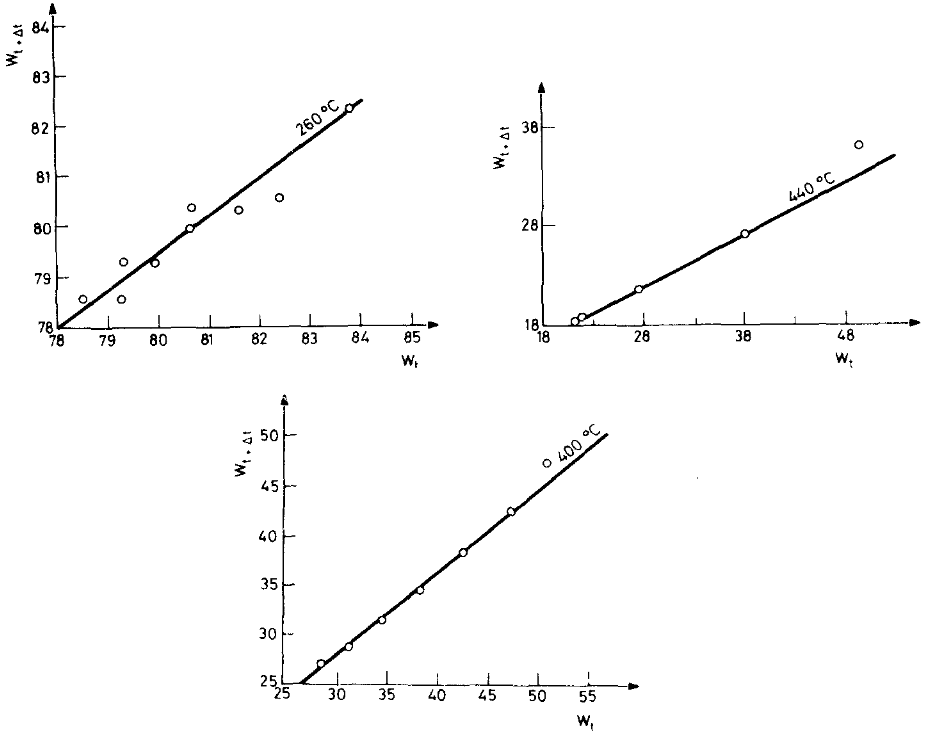


Fig. 4 Plots of W_t *vs.* $W_t + \Delta t$ for the polymer $[Ni(II)(BPTH)_2 \cdot 2H_2O]_n$ using the difference equation method

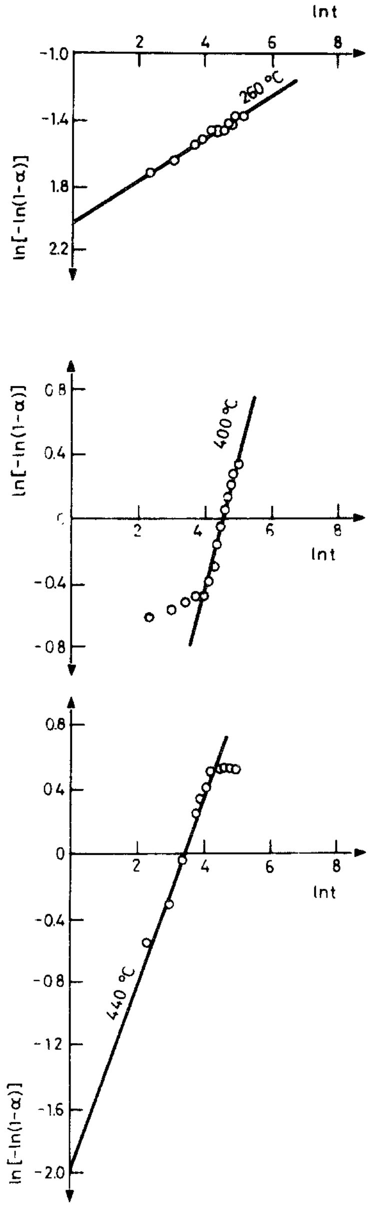


Fig. 5 Avrami–Erofeyev plots for the polymer $[Ni(II)(BPTH)_2 \cdot 2H_2O]_n$

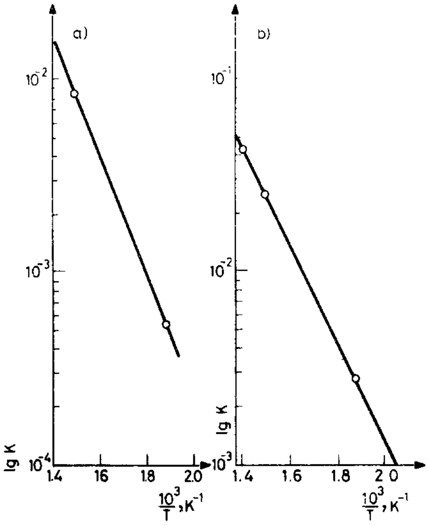


Fig. 6a and 6b Arrhenius plots for the rates of thermal degradaton of [Ni(II)(BPTH)$_2$ · 2H$_2$O]$_n$ using (A) the difference equation method, E_a = 54.69 J/mol; (B) the Avrami–Erofeyev method, E_a = 49.92 J/mol

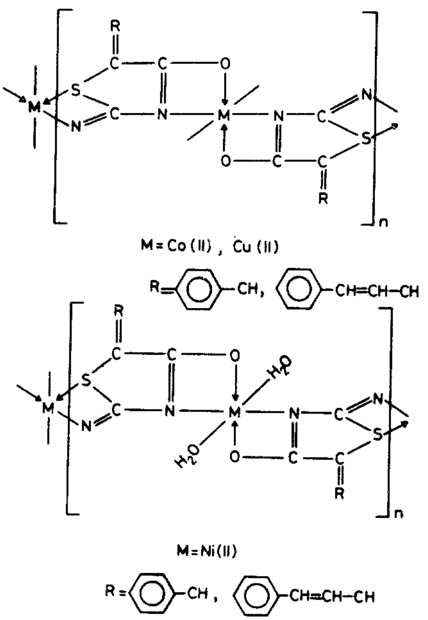


Fig. 7 Tentative structures of the polymeric units for chelate polymers of Co(II), Ni(II) and Cu(II) with BPTH and CPTH

respectively. The corresponding Arrhenius plots are shown in Figs 6a and 6b, respectively. The activation energy was estimated from the Arrhenius plots (Figs 6a and 6b) and are given in Table 3.

The order of the reaction in each step of the thermal degradation was found to be one. A close examination of Table 3 reveals the sequence of thermal stability to be Ni(II) > Cu(II) > Co(II), which is in harmony with that predicted from the non-isothermal TG data. Thus, it has been observed that the kinetic parameters such as activation energy and order calculated from the isothermal TG data using the familiar methods for organic polymers may be used directly to obtain the kinetic parameters for the thermal degradation of chelate polymers.

Table 3 Values of activation energy of degradation of chelate polymers in Joules/mole

No.	Polymer	By difference equation method	Avrami–Erofeyev method
1	$[Co(II)(BPTH)_2]_n$	37.26	36.54
2	$[Ni(II)(BPTH)_2 \cdot 2H_2O]_n$	54.68	49.89
3	$[Cu(II)(BPTH)_2]_n$	22.35	20.49
4	$[Co(II)(CPTH)_2]_n$	24.66	23.05
5	$[Ni(II)(CPTH)_2 \cdot 2H_2O]_n$	51.44	45.77
6	$[Cu(II)(CPTH)_2]_n$	49.95	41.23

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We express our thanks to the Head of the Department of Chemistry, Nagpur University, for providing the necessary facilities. One of the authors (V. N. I.) is thankful to U. G. C., New Delhi for awarding Junior Research Fellowship.

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Zusammenfassung — Koordinationspolymere von Co(II), Ni(II) und Cu(II) mit 5-Benzyliden-pseudothiohydantoin bzw. 5-Cinnamyliden-pseudothiohydantoin als Liganden wurden dargestellt, durch dynamische und statische TG charakterisiert und hinsichtlich der relativen thermischen Stabilität miteinander verglichen. Die durch statische und dynamische TG ermittelte thermische Stabilität stimmen überein. Ausgehend von thermoanalytischen Daten wurde die Struktur der Polymereinheit für jedes Polymer vorausgesagt. Ein Thermogrammtyp — $(ML_2)_n$ — wird für Co(II) und Cu(II) und ein anderer — $(ML_2 \cdot 2H_2O)_n$ — für Ni(II) erhalten. Die statischen (isothermen) TG-Daten wurden nach der Differenzgleichungsmethode und der Avrami–Erofeyev-Methode analysiert. Die Aktivierungsenergien der Zersetzung der Koordinationspolymere wurden berechnet, und es wurde festgestellt, daß Chelatepolymere von Ni(II) mit beiden Ligandtypen stabiler als die entsprechenden Co(II)- und Cu(II)-Komplexe sind. Diese auf Grund von statischen TG-Daten getroffene Voraussage ist in Übereinstimmung mit der, die auf aus dynamischen TG-Kurven berechneten Aktivierungsenergien und Anfangszersetzungstemperaturen beruht.

Резюме — Синтезированы координационные полимеру двухвалентных кобальта, никеля и меди с 5-бензилиден- и 5-циннамилиден-псевдотиогидантоинами. Полученные полимеру были изучены методом динамической и статической ТГ и была сопоставлена их относительная термоустойчивость. Данные динамической и статической ТГ хорошо согласуются друг с другом. На основе термоаналитических данных установлена для каждого полимера структура его полимерного звена. Для полимеров с кобальтом и медью установлено структурное звено типа $(ML_2)_n$, а для никела — $(ML_2 \cdot 2H_2O)_n$. Анализ изотермических ТГ-данных был проведен дифференциальным методом и методом Аврами–Ерофеева. Для координационных полимеров кобальта вычислены энергии активации. Установлено, что хелатные полимеры никеля с обоими лигандами более устойчивы по сравнению с тем, что для кобальта и меди. Найденные явления согласуются с тем, что было установлено для этих же полимеров на основе их энергий активации и начальных температур разложения, вычисленных из кривых динамической ТГ.