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Thermal Studies of Some Transition Metal Complexes of Phenylazoethylacetoacetate

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In the present communication, the authors described the thermal behaviour of phenylazolthylacetoacetate (HPAEA) complexes of Cu (II), Ni (II), Co(II), Fe (II), Pd (II), UO_2 (II) and VO (II) and evaluate some kinetic parameters.

INTRODUCTION

Thermal decomposition and dehydration reactions of transition metal complexes of phenylazoethylacetoacetate (HPAEA) are of great interest. Kinetic studies and calculation of parameters such as enthalpy, order of reaction, thermal stability etc. of such complexes have not been studied earlier. The present studies were carried out to study thermal behaviour of HPAEA complexes with Cu(II), Ni (II), Co (II), Fe (II), Pd (II), UO_2 (II) and VO (II).

EXPERIMENTAL

Analytical grade reagents were used. The ligand, phenylazothylacetoacetate (HPAEA) was prepared by a method as reported in literature[1]. Solid metal chelates were synthesised by refluxing for 2–3 hrs. a mixture of metal salt (50 ml, 0.01 M) in 75% ethanol and HPAEA (50 ml, 0.02 M) in 75% ethanol after raising pH to the appropriate value (Table 1). The resulting coloured complexes precipitated were filtered, washed with alcohol and dried at 80°C. In case of Cu (II) acetate, metal and ligand were mixed in 1 : 1 molar ratio. All the metal chelates were characterised by elemental analysis, magnetic and spectral studies.

RESULTS AND DISCUSSION

All the metal complexes were subjected to thermogravimetric analysis and differential thermal analysis. The data obtained has been used to evaluate kinetic parameters of decomposition of solid complex, order of reaction, activation energy and thermal stability of each complex.

A weighed sample of each complex was heated at a programmed linear rate of 5°C/min. The loss in weight at different temperatures were recorded against the respective temperature of each complex. It was observed that the nature of decomposition involved during the process of heating exhibited two types of reactions (i) successive type of reaction and (ii) simultaneous type of reaction. All the metal complexes exhibited successive type of reactions except for uranyl (II) complex, which exhibited simultaneous type of reaction.

TABLE 1
ANALYTICAL DATA OF COMPLEXES

Sr. No.	Metal complex	M. wt.	pH of formation	μ^*_{eff} (B.M.)	Analysis % found/(calculated)			
					C	H	N	Metal
1.	HPAEA (LH) $C_{12}H_{14}O_3N_2$	234.00	—	—	60.88 (61.53)	5.68 (5.98)	12.14 (11.96)	— —
2.	$CuL_2 \cdot 2H_2O$ (green)	565.50	4.2	1.9	50.92 (5266)	5.30 (4.82)	9.90 (10.21)	11.22 (11.28)
3.	CuLOAc (dark green)	355.50	4.8	1.01	47.25 (46.04)	4.51 (5.62)	7.89 (7.92)	17.81 (17.19)
4.	$NiL_2 \cdot 2H_2O$ (light green)	560.50	5.1	3.1	51.36 (52.24)	5.35 (5.30)	9.98 (9.84)	10.46 (11.09)
5.	$CoL_2 \cdot 2H_2O$ (brown)	561.00	6.8	5.1	51.34 (50.84)	5.82 (5.34)	9.98 (9.87)	10.51 (10.74)
6.	$FeL_2 \cdot 2H_2O$ (brown)	557.80	6.6	5.8	50.61 (51.62)	5.41 (5.37)	10.18 (10.86)	10.14 (10.01)
7.	$PdL_2 \cdot 2H_2O$ (brown)	678.00	7.2	diamagnetic	51.15 (50.03)	4.61 (4.54)	9.98 (9.76)	17.95 (18.58)
8.	UO_2L_2 (yellow)	704.00	7.4	1.4	40.12 (39.12)	3.68 (3.53)	8.02 (7.60)	33.12 (32.34)
9.	VOL_2 (green)	534.00	4.6	1.8	53.98 (54.13)	4.28 (4.88)	10.15 (10.52)	9.75 (10.30)

*At 303 K

All the metal complexes, expect that of Cu (II) acetate and VO (II) sulphate showed first decomposition around 110–130°C, indicating coordinated water molecules are present in these complexes. It was confirmed by the sharp band between 3300 cm^{-1} to 3500 cm^{-1} in the IR spectra of these complexes. Cu (II) acetate and VO (II) complexes of HPAEA do not exhibit these bands in their IR spectra. Most of these complexes decomposed in three stages. The first stage of decomposition of $CuL_2 \cdot 2H_2O$ complex was in the temperature range of 110–130°C corresponding to 6.36% loss, indicating presence of two molecules of water in coordination sphere of metal[2]. In case of Ni (II), Co (II), Fe (II) and Pd (II) complexes weight losses were 7.58%, 6.31%, 7.04% and 5.78% corresponding to two molecules of water in respective complex.

Second stage of decomposition for $CuL_2 \cdot 2H_2O$ complex was found broadly in the range of 150 to 190°C corresponding to loss of 37.1% in the weight. This was attributed to loss of two $C_6H_5N_2$ (azo) groups. This indicates that two azo groups were linked to metal forming octahedral structure which was already confirmed by analytical data[3]. Percentage loss in weight at second and third stage of decomposition of Ni (II), Co (II), Fe (II) and Pd (II) complexes were 37.9%, 43.34%, 44.2% and 37.9% respectively corresponding to $C_6H_5N_2$ (azo) groups present in each complex. Second stage decomposition in all these complexes occured in the temperature range of 170°–220°C. From this data, it was concluded that a metal atom and nitrogen from azo (hydrazino) group of ligand were bonded in complex which were found fissionable at an early stage compared to that of metal oxygen bond[2].

DTA peak obtained at second stage decomposition was observed in the range of 200°–225°C as an exothermic peak in each case.

Third stage of decomposition of $CuL_2{\cdot}2H_2O$ complex was in the temperature range of 420°–510°C showing weight loss of 76.3%, which corresponds to loss of two methyl (CH_3), two ethyl (C_2H_5) and two-CO_2 groups. This was also supported the fact that the CH_3CO group, from the ligand HPAEA was linked to metal by coördinate bonding to form octahedral structure[4]. Involvement of oxygen of CH_3CO group to form coordinate bond with metal atom was already proved by IR spectra of the complex[4]. Percentage weight loss of Ni (II), Cu (II), Fe (II) and Pd (II) complexes in the temperature range 350°–460°C found were 76.7%, 76.65%, 76.02% and 70.05% respectively corresponding to loss of two ethyl, two methyl and two CO_2 groups in each case. This indicated that all these complexes acquired similar octahedral structures as that of $CuL_2{\cdot}2H_2O$. The DTA peaks in third stage decomposition for all these complexes were found in temperature range 320°–450°C and were exothermic in nature.

The final decomposition products or residues of these complexes of HPAEA (>550°C) were found to be oxides of respective metals, such as CuO, NiO, CoO, Fe_2O_3 and PdO. These were confirmed by weight loss data obtained from independent pyrolysis experiment in which complexes were heated in silica crucible to 700°C in air. These weight losses were in good agreement with thermogravimetric data confirming purity of complexes[5].

The complex of Cu (II) acetate decomposes in two stages. It was thermally stable around 180°–190°C indicating the absence of coordinated water molecules in the coordination sphere of the metal. It was confirmed by absence of a peak around 3500 cm^{-1} in the IR spectra of this complex[6]. The first stage decomposition of this complex was observed at the temperature 220°C, corresponding to 47.76% weight loss and indicating loss of two acetato and two diazo ($C_6H_5N_2$) groups. This was in good agreement with proposed structure involving metal acetate and metal hydrazone linkage forming dimeric square planar structure[7]. DTA peak at this temperature was exothermic.

Second stage decomposition was found in the temperature range of 300–380°C which corresponds to 70.88% weight loss. This was explained by decomposition of two ethyl, two methyl and two-CO_2 groups which suggests that $-CH_3CO$ groups were bonded with metal atom. DTA peak in this temperature region was also found exothermic. Decomposition was completed at around 500°C involving loss of 77.65% and residue was left behind as CuO.

The vanadyl complex decomposed in three stages. First stage of decomposition was observed at 310°C showing loss of 20.54% due to loss of an azo group ($C_6H_5N_2$) and one N_2 molecule. This indicated linkage of hydrazone group of regent HPAEA with vanadyl (II) group forming square pyramidal structure[8,9]. DTA peak in this region was found to be exothermic. Second stage of decomposition was observed between 430°–450°C showing weight loss of 55.65% corresponding to loss of two CH_3CO groups and a phenyl (C_6H_5) group proving their involvement with vanadyl VO (II) group in coordinate bond formation. In this region DTA peak was found to be exothermic. Third stage of decomposition was observed between 700°–750°C corresponding to 82.67% loss in weight which could be attributed to loss of two ethyl and two CO_2 gropus. DTA peak in this region was found exothermic.

Order of decomposition reaction was calculated by use of Freeman-Caroll's equation. The reaction mechanism of decomposition was not found to change with change in temperature. In such cases, the graph of fraction of weight loss versus time showed nature of Arrhenius plots and they are used to calculate the order of reaction and activation energy (E_a) of thermal decomposition.

The difference differential method of Freeman-Carroll[10] was used for evaluating the kinetic parameters from thermogravimetric data. The equation used in the method is:

$$\frac{dw}{dt} = \frac{Z}{HR} \cdot e^{-Ea/RT} (W)^n \tag{1}$$

W = fraction decomposed.
E_a = activation energy
n = order of reaction
R = rate constants
T = temperature in absolute scale

In lograthmic terms equation (1) becomes:

$$\Delta \log \frac{dw}{dt} = n\Delta \log w - \left[\frac{E_a}{2.303\,R}\right] \Delta\left[\frac{1}{T}\right]$$

Hence plot of:

$$\frac{\Delta \log \frac{dw}{dt}}{\Delta \log W} \text{ Versus } \frac{\Delta\left(\frac{1}{T}\right)}{\Delta \log W}$$

should provide linear relationships. Slope of this enables us to calculate activation energy (E_a) and intercept provides *a*, the order of reaction which was found to be 1 : 1 for $CuL_2{\cdot}2H_2O$. For octahedral complexes of Ni (II), Co (II), Fe (II) and Pd (II) orders were found to be 2.2, 0.75, 2.8 and 1.2 respectively. Activation energy for octahedral $CuL_2{\cdot}2H_2O$ complex was found to be 1.2 K. cal/mole whereas for Ni (II), Co (II), Fe (II) and Pd (II) values were found to be 5.7, 9.4, 2.8 and 1.35 K.cal/mole respectively. For dimeric square planar complex of Cu(II) acetate activation energy was found to be 2.14 K. cal/mole and order of reaction was found to be 2.0. VOL_2 has square pyramidal structure and its activation energy was found to be 0.207 K.cal/mole, and order of reaction was 1.2.

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