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Thermodecomposition Kinetics of La(III) Complex with Schiff Base Ligand Derived from Glycine and O-Vanillin

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A new Schiff base complex has been synthesized and characterized by elemental analyses, IR and molar conductance. Thermodecomposition kinetics of the complex were investigated under non-isothermal condition. TG and DTG curves indicate the complex decomposes in three steps. The kinetics of step(1) and (3) were calculated by a combination of Achar differential and Coats-Redfern integral methods. The kinetic equations may be expressed as: step (1): $d\alpha/dt = Ae^{-E/RT}(1-\alpha)^2$; step (3): $d\alpha/dt = Ae^{-E/RT}/2(1-\alpha)^3$.

Key Words: Thermodecomposition, Kinetics, La(III) Complex, Schiff base ligand, Glycine, O-Vanillin.

INTRODUCTION

Some Schiff base complexes derived from amino acids are particularly active in biological system. Recently, studies of such complexes of transition metal ions with Schiff base have been reported[1-3]. To continue the investigation in this area, the La(III) complex of Schiff base derived from glycine and O-vanillin was synthesized. As thermal aspects are essential to the complex, the thermodecomposition process of $[La(C_{10}H_{13}N_3O_{10})]NO_3\cdot 2H_2O$ by TG-DTG is described in this paper and the corresponding non-isothermal kinetics are discussed.

EXPERIMENTAL

Glycine was biochemical reagent (BR) the other reagents were analysis reagent (AR) grade and were used without further purification.

Elemental analyses were carried out with a model 2400 Perkin-Elmer analyzer. Infrared spectrum was recorded in KBr pellets using a Nicolet 170 SX spectrophotometer in the 4000-400 cm^{-1} region. Molar conductivity at room temperature was measured in 10^{-3} M DMSO solution using a DDS-11A type conductivity meter at 25 ºC. The thermogravimetric measurements were made using a Perkin-Elmer TGA 7 thermogravimeter. The heating rate was programmed to be 10 ºC/min with the protecting stream of N_2 flowing at 40 mL/min.

Preparation of the ligand: O-vanillin was added (with stirring) to anhydrous ethanol (20 mL) to make a pellucid solution. Then, it was slowly dripped into the anhydrous ethanol solution (15 mL) containing 0.01 mol glycine (containing 0.01 mol KOH) at 65 ºC ((pH = 6.0~6.5), a mass of yellow grain was separated out which was collected by filtration and washed several times with anhydrous ethanol, recrystallized with methanol and then dried under vacuum (Yield 85.2 %). Anal. Calcd. (found) (%): C 48.53 (48.53), H 4.08 (4.15), N 5.58 (5.58). IR (KBr, cm^{-1}): 1660 ν(C=N), 1603, 1314 ν(COO^-), 1242 ν(Ar-O).

Preparation of the complex: 0.5 mmol of lanthanide(III) nitrate hexahydrate in 15 mL of anhydrous ethanol was added dropwise into the solution of Schiff base (0.5 mmol) in 15 mL of anhydrous ethanol and was stirred at 80 ºC. The yellow solution obtained was filtered and the yellow powder was dried under vacuum. The C, H and N contents were as follows: Anal. Calcd. (found) (%): C 20.99 (20.23), H 2.99 (2.80), N 9.79 (9.67), La 24.28 (21.75). IR (KBr, cm^{-1}): 1645 ν(C=N), 1592, 1381 ν(COO^-), 1211 ν(Ar-O).

La(III) complex is yellow powder, soluble in DMSO, DMF. The molar conductivity of the complex is 83.33 W^{-1} cm^2 mol^{-1} in DMSO. Molar conductivity for the complex in DMSO corresponds to electrolytes[4].

The infrared studies indicate the shift of ν(C=N) from 1660 cm^{-1} in the ligand to 1645 cm^{-1} in the complex, suggests that La^{3+} is bonded with N-atom in Schiff base. The shift of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ from 1603 and 1314 cm^{-1}, respectively in the ligand to 1592 and 1381 cm^{-1} in the complex, respectively, suggests the coordination of the oxygen in the carboxylate group to the metal ion. The value of $\nu[\nu_{as}(COO^-)-\nu_s(COO^-)] = 211$ cm^{-1} indicates that the -COO^- group is coordinated to the metal ion in a monodentate fashion[5]. A broad absorption band at the range of 3300-3000 cm^{-1} confirms the presence of water in the complex. The appearing of (Ar-O) (1211 cm^{-1}) is lower than 1242 cm^{-1}, which exposes that Ar-O-La in the complex. In the spectrum of the complex, five additional bands, which are not present in the spectrum of the free ligand, were observed. The bands at 1391 and 1261 cm^{-1} are assigned to the metal ion in the non-coordination. The nitrate vibration of complex is seen as split bands at 1539-1531, 1236-1225 and 1062-1026 cm^{-1}. The separation of modes has been used as a criterion to distinguish between mono- and bidentate chelating nitrates. The magnitude of this separation may be indicative of a bidentate interaction of the nitrate anions with the lanthanide ions[6].

Thermal decomposition studies: The TG and DTG curves of the complex are shown in Fig. 1, which indicate that complex decomposes in

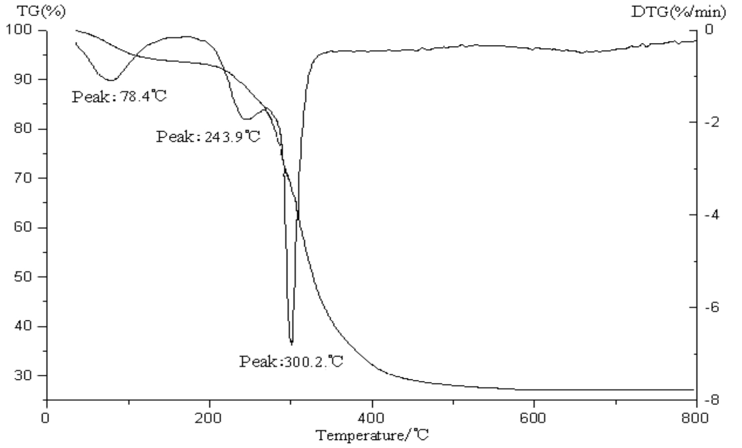

Fig. 1. TG-DTG curves of the complex

three steps. The first weight loss stage has decomposition temperature ranges of 25-115 ºC, with weight losses of 6.62 % (calcd. 6.31 %), which corresponds to the losses of two molecules of water. The second weight loss stage has decomposition temperature range of 115-280 ºC, corresponding to the fractional losses of the nitrate ion of outer of the coordination sphere with weight losses of 11.02 % (calcd. 10.87 %). The third weight loss stage showed a continuous weight loss between 280-800 ºC, which corresponds to the loss of all of the ligand and 27.6 % of the original sample remained. With its calculated weight percentage of 28.42 %, La_2O_3 is the final product.

On the basis of 30 kinetic functions in both differential and integral forms commonly used in recent reviews[7,8], the non-isothermal kinetics of the steps were investigated using the Achar differential method and the Coats-Redfern integral method.

The original kinetic data for step (1) and (3) obtained from the TG and DTG curves are listed in Tables 1 and 2, respectively, in which T_i is the temperature at any point i on the TG and DTG curves, ai is the corresponding decomposition rate. $(d\alpha/dt)_i = [\beta/(W_0-W_1)] \times (dw/dt)_i$ in which $(dw/dt)_i$ is the height of the peak in the DTG curve, β is the heating rate and W_0 and W_1 are the initial and final weight at that stage, respectively.

The calculated kinetic parameters (E, A) and correlation coefficients (r) of step (1) and (3) are listed in Tables 3 and 4.

The results obtained from the two different methods are approximately the same when based on function No. 23 for step (1) and function No. 3 for step (3). The kinetic equations are expressed as follows: step (1): $d\alpha/dt = Ae^{-E/RT} (1-\alpha)^2$; step (3): $d\alpha/dt = Ae^{-E/RT} /2(1-\alpha)^3$.

TABLE-1
DATA FOR STEP (1) OF THE THERMODECOMPOSITION OF THE COMPLEX OBTAINED FROM THE TG AND DTG CURVES

T_i (K)	α_i	$d\alpha/dt$
331	0.1909	0.2573
335	0.2361	0.2912
339	0.2850	0.3129
342	0.3231	0.3228
346	0.3751	0.3348
351	0.4427	0.3455
357	0.5233	0.3340
361	0.5751	0.3124
365	0.6216	0.2866

TABLE-2
DATA FOR STEP (3) OF THE THERMO DECOMPOSITION OF THE COMPLEX OBTAINED FROM THE TG AND DTG CURVES

T_i (K)	α_i	$d\alpha/dt$
553	0.1390	0.1829
558	0.2406	0.2696
563	0.3938	0.3268
568	0.4465	0.3911
573	0.5598	0.3564
578	0.6678	0.3071
583	0.7312	0.2641
588	0.7681	0.1812
593	0.7913	0.0901

The activation entropy and activation free-energy ΔG are calculated by the following equations[8]:

$$A = kT_s/ h\exp(\Delta S/R)$$
$$Ae^{-E/RT} = kT_s/h\exp(\Delta S/R)\exp(-\Delta H/RT)$$
$$\Delta G = \Delta H - T\Delta S$$

T_s is the temperature at the top of peak, k is Boltzmann constant, R is gas constant, h is Plank constant. The activation entropy ΔS and activation free-energy ΔG for the first and the third thermal decomposition stage were obtained, step (1): ΔS = -153.66 J/mol K, = 103.83 kJ/mol, step (3): ΔS = 487.19 J/mol K, = -46.31 kJ/mol.

According to the characterizations enumerated above, the possible structure of the complex is shown as Fig. 2.

TABLE-3
RESULTS OF THE ANALYSIS OF THE DATA FOR STEP (1) BY THE ACHAR DIFFERENTIAL METHOD AND THE INTEGRAL METHOD COATS-REDFERN

E (kJ/mol)	ln (A/S^{-1})	r	E (kJ/mol)	ln (A/S^{-1})	r
37.62	11.56	0.9569	63.24	8.22	0.9913
47.85	14.67	0.9780	69.37	9.82	0.9938
51.73	14.60	0.9831	71.71	9.18	0.9946
59.27	17.39	0.9896	76.40	10.92	0.9960
28.12	5.74	0.9266	56.60	3.50	0.9891
81.87	25.76	0.9977	91.47	16.50	0.9986
25.71	8.28	0.9868	38.96	1.06	0.9970
10.80	2.95	0.9569	24.04	-3.86	0.9965
3.35	0.20	0.7651	16.59	-6.32	0.9957
-4.11	-2.66	0.8668	9.13	-8.78	0.9934
-7.84	-4.18	0.9645	5.40	-10.01	0.9890
14.41	3.40	0.9288	33.58	-1.63	0.9940
18.18	4.39	0.9609	35.31	-1.39	0.9952
3.11	-0.09	0.3924	28.73	-2.74	0.9893
-14.14	-6.27	0.9376	11.47	-8.22	0.9828
-19.90	-8.50	0.9746	5.72	-10.05	0.9689
-22.77	-9.70	0.9831	2.85	-10.96	0.9310
48.32	16.65	0.9996	51.33	5.63	0.9997
37.02	11.77	0.9973	5.52	-9.52	0.9658
-8.39	-4.15	0.8170	17.22	-6.39	0.9866
70.45	23.73	0.9950	83.69	15.82	0.9975
115.19	38.90	0.9962	128.43	30.58	0.9976
159.93	53.95	0.9967	173.17	45.34	0.9977
70.92	25.71	0.9995	39.43	3.04	0.9880
20.06	4.80	0.9705	36.20	-1.35	0.9957
-19.49	-7.77	0.8825	20.56	-5.10	0.9733
-42.10	-15.74	0.9523	14.21	-7.10	0.9436
-64.70	-23.82	0.9686	9.37	-8.66	0.8903
-2.37	-2.46	0.5514	14.76	-7.55	0.9928
5.78	-0.04	0.7741	13.90	-7.67	0.9909

TABLE-4
RESULTS OF THE ANALYSIS OF THE DATA FOR STEP (3) BY THE ACHAR DIFFERENTIAL METHOD AND THE INTEGRAL METHOD COATS-REDFERN

E (kJ/mol)	ln (A/S^{-1})	r	E (kJ/mol)	ln (A/S^{-1})	r
69.55	13.12	0.4964	211.69	30.22	0.9289
113.88	22.12	0.6821	236.76	35.03	0.9406
131.91	24.56	0.7354	246.94	35.75	0.9450
166.33	32.07	0.8088	267.58	40.26	0.9526
37.17	3.70	0.3077	188.93	22.95	0.9210
269.59	54.62	0.9139	336.41	55.30	0.9702
62.20	12.51	0.6131	145.41	17.46	0.9597
10.56	1.39	0.1548	93.77	6.74	0.9571
-15.27	-4.26	0.2421	67.95	1.38	0.9541
-41.09	-10.03	0.5970	42.12	-3.98	0.9473
-54.00	-12.99	0.7180	29.21	-6.66	0.9389
10.57	0.55	0.1299	121.45	11.53	0.9433
27.78	3.90	0.3263	129.03	12.78	0.9493
-41.06	-10.04	0.4493	101.09	7.76	0.9227
-96.36	-21.96	0.8382	45.78	-3.47	0.9077
-114.79	-26.11	0.8965	27.35	-7.21	0.8884
-124.01	-28.27	0.9173	18.13	-9.09	0.8628
165.46	35.06	0.9000	204.34	30.31	0.9810
113.83	23.10	0.8183	42.11	-3.43	0.9918
-77.93	-17.93	0.7493	64.22	0.27	0.9157
217.13	45.37	0.8746	300.35	49.62	0.9622
372.07	77.93	0.9171	455.28	81.78	0.9630
527.00	110.38	0.9328	610.21	113.94	0.9633
268.71	58.31	0.9569	196.99	30.40	0.9939
36.39	5.49	0.4124	132.97	13.35	0.9521
-144.31	-31.89	0.8629	69.93	1.59	0.8706
-247.57	-54.04	0.9414	48.72	-2.71	0.8084
-350.83	-76.30	0.9660	34.24	-5.68	0.7406
-41.49	-10.54	0.5600	59.75	-0.96	0.9414
-17.08	-5.76	0.2333	55.96	-1.59	0.9340

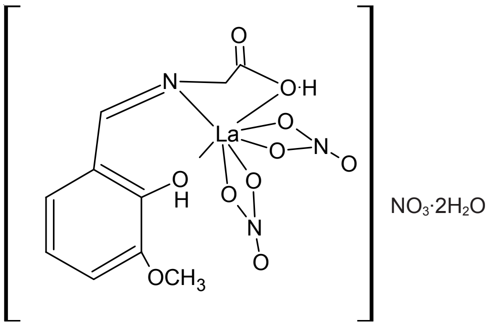

Fig. 2. Suggested structure of the complex

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