

Thermodecomposition Kinetics of Cu(II) Complex with Schiff Base Ligand

ZHEN JIA

Department of Chemistry, Dezhou University, DeZhou-253023, P.R. China

E-mail: jixiangtian115@163.com

A new Schiff base complex of Cu(II) has been synthesized and characterized by elemental analyses, IR and molar conductance. The thermodecomposition kinetics of the complex was investigated under non-isothermal condition TG and DTG curves indicate the complex decomposes in two steps. The kinetics of step (1) and (2) were calculated by a combination of Achar differential and Coats-Redfern integral methods.

Key Words: Thermodecomposition, Kinetics, Cu(II) complex, Schiff base.

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 been reported¹⁻³. Present study reports the synthesis of Cu(II) complex of Schiff base derived from glycine and 2,4-dihydroxybenzaldehyde. As thermal aspects are essential to the complex, the thermodecomposition process of $[\text{Cu}_2(\text{C}_9\text{H}_7\text{NO}_4)_2] \cdot 2\text{H}_2\text{O}$ by TG-DTG is also described and the corresponding non-isothermal kinetics are discussed.

EXPERIMENTAL

Glycine was Biochemical Reagent while the other reagents were 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 170SX spectrophotometer in the 4000-400 cm^{-1} region. Molar conductivity at room temperature was measured in 10^{-1} M DMSO solution using a DDS-11A type conductivity meter at 25 °C. Thermogravimetric measurements were made using a Perkin-Elmer TGA7 thermo gravimeter. The heating rate was programmed to be 10 °C/min with the protecting stream of N_2 flowing at 40 mL/min.

Preparation of the ligand: 2,4-Dihydroxybenzaldehyde 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 °C, 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 for later use. The yield of the reaction was 82.3 %. Anal. Calcd. for C, 46.34 %; H, 3.46 %; N, 6.00 %;. Found: C, 46.34 %; H, 3.86 %; N, 6.12 %. IR data (KBr pellets, cm^{-1}): 1649 $\nu(\text{C}=\text{N})$; 1614, 1351 $\nu(\text{COO}^-)$; 1225 $\nu(\text{Ar}-\text{O})$.

Preparation of the complex: 0.5 mmol of cupric acetate 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 70 °C. The dark green solution obtained was filtered and the dark green powder was dried under vacuum. The C, H and N contents were as follows: Anal. Calcd. for C, 39.35 %; H, 3.30 %; N, 5.10 %; Cu, 23.13 %. Found: C, 39.90 %; H, 3.11 %; N, 5.20 %; Cu, 24.05 %. IR data (KBr pellets, cm^{-1}): 1636 $\nu(\text{C}=\text{N})$; 1601, 1368 $\nu(\text{COO}^-)$; 1219 $\nu(\text{Ar}-\text{O})$; 512 $\nu(\text{Cu}-\text{N})$; 496 $\nu(\text{Cu}-\text{O})$.

RESULTS AND DISCUSSION

Molar conductance and spectroscopic studies: The present complex is green powder, soluble in DMSO and DMF. The molar conductivity of the complex is $12.24 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in DMSO. Molar conductivity for the complex in DMSO corresponds to nonelectrolyte⁴.

The shift of $\nu(\text{C}=\text{N})$ from 1649 cm^{-1} in the ligand to 1636 cm^{-1} in the complex, suggests that Cu ion is bonded with N atom in Schiff-base. The shift of $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ from 1614 and 1351 cm^{-1} in the ligand to 1601 and 1368 cm^{-1} in the complex, respectively, suggests the coordination of the oxygen in the carboxylate group to the metal ion. A broad absorption band at the range of $3300\text{-}3000 \text{ cm}^{-1}$ confirms the presence of water in the complex. The appearing of Ar-O frequency (1219 cm^{-1}) is lower than 1225 cm^{-1} , which exposes that Ar-O-Cu in the complex.

Thermal decomposition studies: The TG and DTG curves of the complex are shown in Fig. 1, which indicate that complex decomposes in two steps. The first weight loss stage has decomposition temperature ranges of $35\text{-}110 \text{ }^\circ\text{C}$, with weight losses of 7.13 % (calcd. 6.58 %), which corresponds to the losses of two molecules of water. The second weight loss stage has decomposition temperature range of $110\text{-}800 \text{ }^\circ\text{C}$, corresponding to the fractional losses of Schiff base ligand with weight losses of 62.07 % (calcd. 64.67 %). CuO is the final product.

On the basis of 30 kinetic functions in both differential and integral forms commonly used in recent reviews^{5,6}, 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 (2) 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, α_i 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.

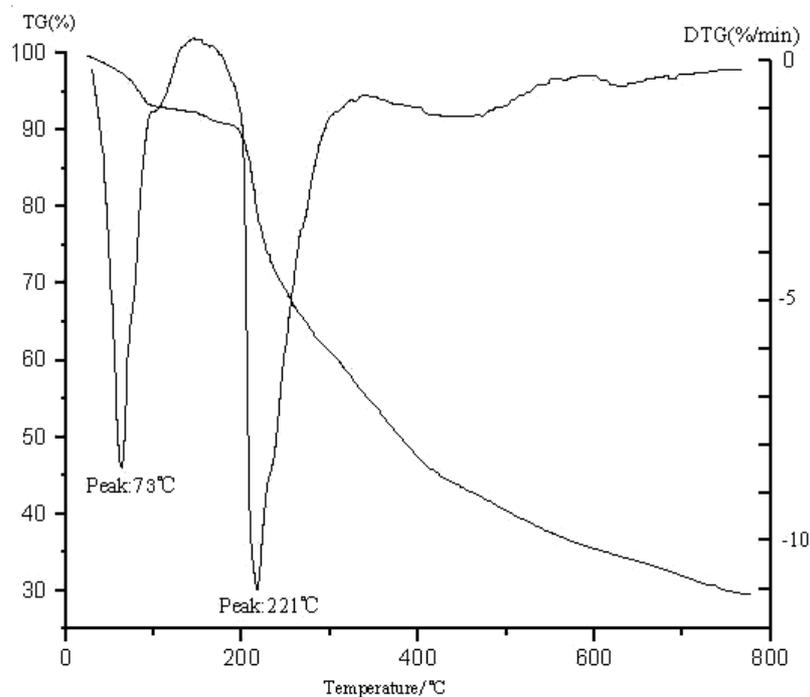


Fig. 1. TG-DTG curves of the complex

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

T_i (K)	α_i	$d\alpha/dt$
324	0.0957	0.2870
329	0.1395	0.3422
334	0.1987	0.4004
337	0.2431	0.4556
341	0.3124	0.5010
346	0.4121	0.5205
351	0.5125	0.4986
356	0.5917	0.4419
359	0.6330	0.3847
362	0.6723	0.3518
367	0.7306	0.3330

The calculated kinetic parameters (E , A) and correlation coefficients (r) of step (1) and (2) are listed in Tables 3 and 4.

The results obtained from the two different methods are approximately the same when based on function No.18 for step (1) and function No. 23 for step (2). The kinetic equations are expressed as follows: step (1): $d\alpha/dt = Ae^{-E/RT} (1-\alpha)^2$, step (2): $d\alpha/dt = Ae^{-E/RT} 1/4(1-\alpha)[-ln(1-\alpha)^{-3}]$.

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

T_i (K)	α_i	$d\alpha/dt$
468	0.2712	0.0583
573	0.2837	0.0795
578	0.3000	0.1860
584	0.3588	0.5442
589	0.4342	0.6234
594	0.5135	0.6548
599	0.5949	0.6207
503	0.6544	0.5710
508	0.7231	0.5281
512	0.7750	0.5139
513	0.7880	0.5112

TABLE-3
RESULTS OF THE ANALYSIS OF THE DATA FOR STEP (1) IN TABLE 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
49.38	15.91	0.9126	88.86	17.11	0.9807
62.29	19.99	0.9523	96.51	19.25	0.9854
67.28	20.33	0.9626	99.46	18.84	0.9870
76.92	23.89	0.9762	105.40	21.04	0.9898
37.74	9.32	0.8622	80.74	11.85	0.9767
105.82	34.56	0.9938	124.67	28.15	0.9957
30.99	10.49	0.9685	54.48	6.49	0.9923
10.92	3.36	0.8796	34.41	-0.24	0.9913
0.88	-0.29	0.1759	24.37	-3.60	0.9901
-9.15	-4.06	0.9149	14.34	-6.96	0.9870
-14.17	-6.03	0.9686	9.32	-8.64	0.9824
16.53	4.46	0.8406	47.64	3.27	0.9862
21.35	5.83	0.9098	49.83	3.67	0.9885
2.08	-0.18	0.1530	41.57	1.71	0.9778
-21.57	-8.57	0.9197	17.92	-5.99	0.9699
-29.45	-11.55	0.9665	10.03	-8.55	0.9573
-33.39	-13.12	0.9778	6.09	-9.84	0.9357
59.89	21.16	0.9978	70.47	12.38	0.9986
45.44	15.13	0.9926	8.72	-8.35	0.9503
-13.68	-5.72	0.7904	25.80	-3.42	0.9743
91.2	31.36	0.9876	114.69	26.67	0.9931
151.41	51.94	0.9904	174.90	46.84	0.9934
211.62	72.41	0.9915	235.11	67.02	0.9935
88.80	32.53	0.9976	52.08	7.66	0.9756
23.76	6.44	0.9313	50.96	3.80	0.9895
-26.82	-10.16	0.8134	31.54	-1.33	0.9540
-55.73	-20.43	0.9124	23.93	-3.78	0.9209
-84.63	-30.81	0.9395	18.17	-5.67	0.8792
-6.43	-3.54	0.7189	22.05	-5.01	0.9850
4.71	-0.08	0.4831	20.95	-5.21	0.9818

TABLE-4
RESULTS OF THE ANALYSIS OF THE DATA FOR STEP (2) IN TABLE 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
158.99	35.52	0.9039	109.11	11.14	0.9911
186.54	41.54	0.9393	124.66	14.25	0.9912
197.77	42.76	0.9501	130.99	14.29	0.9910
219.19	47.97	0.9655	143.82	17.42	0.9904
139.63	28.45	0.8743	95.46	5.51	0.9909
283.46	63.59	0.9889	186.67	27.83	0.9871
164.37	37.62	0.9405	77.77	5.03	0.9879
135.56	30.70	0.9081	48.96	-1.48	0.9865
121.16	27.15	0.8838	34.56	-4.74	0.9849
106.75	23.49	0.8514	20.15	-8.00	0.9807
99.55	21.57	0.8312	12.95	-9.63	0.9743
132.24	29.11	0.8887	62.87	0.71	0.9897
142.95	31.31	0.9097	67.58	1.45	0.9893
100.10	22.00	0.7916	50.22	-1.69	0.9896
70.66	14.89	0.6689	20.78	-8.10	0.9850
60.85	12.35	0.6103	10.97	-10.24	0.9766
55.94	10.99	0.5768	6.06	-11.31	0.9583
228.64	53.23	0.9830	114.49	13.93	0.9811
196.51	44.73	0.9681	23.47	-6.70	0.9258
80.48	17.32	0.7176	30.60	-5.96	0.9876
250.81	57.85	0.9801	164.21	24.58	0.9890
337.24	77.80	0.9916	250.64	44.12	0.9894
423.68	97.63	0.9956	337.08	63.66	0.9895
292.91	69.55	0.9949	119.88	16.73	0.9518
148.31	32.32	0.9187	70.03	1.76	0.9890
35.84	7.07	0.3505	30.98	-5.73	0.9811
-28.43	-8.14	0.2409	18.09	-8.55	0.9555
-92.70	-23.47	0.5704	9.55	-10.44	0.8926
104.83	22.64	0.8365	29.46	-6.53	0.9861
117.52	25.21	0.8629	27.10	-6.90	0.9864

The activation entropy ΔS and activation free-energy ΔG are calculated by the following equations⁶:

$$A = kT_s / h \exp(\Delta S/R)$$

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

$$\Delta G = \Delta H - T\Delta S$$

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): $\Delta S = -106.72$ mol K, $\Delta G = 227.04$ kJ/mol, step (2): $\Delta S = 420.93$ J/mol K, $\Delta G = 159.81$ kJ/mol.

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

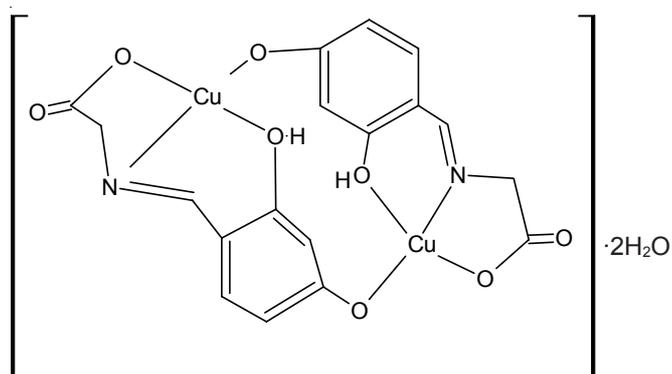


Fig. 2. Suggested structure of the complex

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