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STUDIES ON THE NON-ISOTHERMAL KINETICS OF THE THERMAL DECOMPOSITION OF $[Cu(NBOCTB)][Cu(NO_3)_4]\cdot H_2O$

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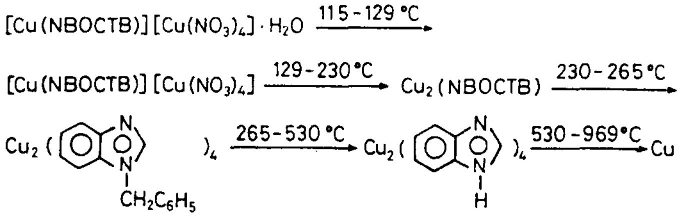
Abstract

The thermal decomposition process of the complex $[Cu(NBOCTB)][Cu(NO_3)_4]\cdot H_2O$ has been studied by TG and DTG technique, and possible intermediates of the thermal decomposition have also been conjectured from the TG and DTG curves. The results suggest that the decomposition of the complex involves five steps:



The non-isothermal kinetics of steps 1, 2 and 3 have been studied by means of the Achar and Coats-Redfern method based on TG and DTG curves. Step 1 is a 'Coring and Growth' mechanism ($n=1$), its kinetic equation may be expressed as: $d\alpha/dt=Ae^{-E/RT}(1-\alpha)$. Steps 2 and 3 are both 'two order chemical reaction' mechanisms, their kinetic equations can be expressed as: $d\alpha/dt=Ae^{-E/RT}(1-\alpha)^2$.

Keywords: copper compound, coupled technique, kinetics, macrocyclic complex, non-isothermal.

Introduction

There has been recent interest in the study of macrocyclic complexes containing copper atoms as possible models for biochemically important proteins and enzymes [1]. It has been generally accepted that imidazole groups play an important role in the coordination chemistry of the copper ion in many copper-containing proteins [2]. This paper reports the possible process and mechanism of thermal decomposition of the complex of copper(II) with N, N, N′, N′-tetra-[(1′-benzyl-2′-benzimidazol) methyl]-

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trans-1,2-diaminocyclohexane (NBOCTB), [Cu(NBOCTB)][Cu(NO_3)$_4$]·H_2O determined on the basis of non-isothermal TG and DTG curves.

Experimental

Preparation of [Cu(NBOCTB)][Cu(NO_3)$_4$]·H_2O

The ligand NBOCTB was prepared as described in [3]. To a DMF solution (50 ml) of NBOCTB (0.25 mmol) in a solution (10 ml) of Cu(NO_3)$_2$ (2 mmol) in ethanol was added with constant stirring under reflux in about 5 min. The resulting green solution was allowed to dry at room temperature in air for about a week to give green crystals of the complex [Cu(NBOCTB)][Cu(NO_3)$_4$]·H_2O. Single-crystal X-ray diffraction analysis confirmed its molecular formula to be [Cu(NBOCTB)] [Cu(NO_3)$_4$]·H_2O.

Experimental equipment and conditions

The TG and DTG curves were obtained using a Perkin-Elmer model TGS-2 thermobalance in the temperature range 40–980°C. The heating rate was 5°C min^{-1} and the flow rate of N_2 gas was 20 ml min^{-1}. The amount of sample used was 3.6568 mg.

Results and discussion

Thermal decomposition process

The TG and DTG curves of [Cu(NBOCTB)][Cu(NO3)4]·H2O are shown in Fig. 1.

On the basis of the TG and DTG curves, the thermal decomposition of [Cu(NBOCTB)][Cu(NO_3)$_4$]·H_2O was assumed to proceed as shown in Table 1. Non-isothermal kinetics for Steps 1, 2 and 3.

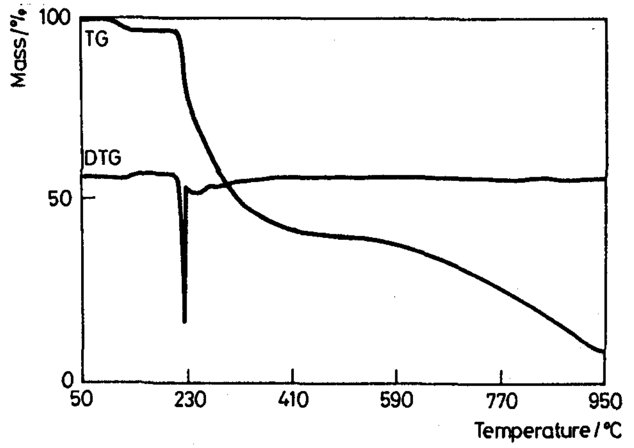
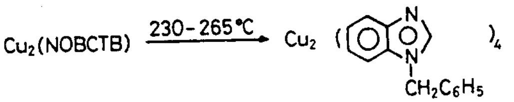
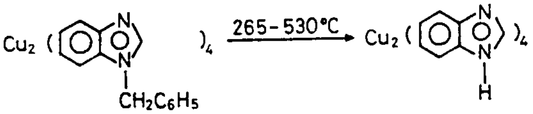
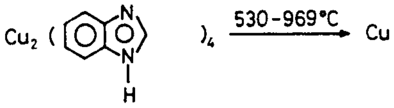


Fig. 1 TG and DTG curves of [Cu(NBOCTB)][Cu(NO_3)$_4$]·H_2O

Table 1 Thermal decomposition process of $[Cu(NBOCTB)][Cu(NO_3)_4]\cdot H_2O$

Step	Decomposition process	Mass loss/%[a]
1	$[Cu(NBOCTB)][Cu(NO_3)_4]\cdot H_2O \xrightarrow{115-129°C} [Cu(NBOCTB)][Cu(NO_3)_4]$	1.40 (1.30)
2	$[Cu(NOBCTB)][Cu(NO_3)_4] \xrightarrow{129-230°C} Cu_2(NBOCTB)$	18.81 (17.86)
3		11.52 (11.77)
4		26.21 (25.93)
5		33.16 (33.99)

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[a] Values in paratheses are calculated values

Table 2 Kinetic functions used for the analysis

Function No.	Differential form, $f(\alpha)$	Integral form, $g(\alpha)$
1	$1/2\alpha$	α^2
2	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$
3	$3[(1-\alpha)^{-1/2}-1]^{-1}/2$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
4	$3(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}/2$	$[1-\ln(1-\alpha)^{1/3}]^2$
5	$(1-\alpha)$	$-\ln(1-\alpha)$
6	$3(1-\alpha)[-\ln(1-\alpha)]^{1/3}/2$	$[-\ln(1-\alpha)]^{1/1.5}$
7	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
8	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
9	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
10	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
11	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
12	1	α
13	$2\alpha^{1/2}$	$\alpha^{1/2}$
14	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
15	$2(1-\alpha)^{3/2}$	$(1-\alpha)^{-1/2}$

Achars equation [4]

$$\ln[(\mathrm{d}\alpha/\mathrm{d}t)/f(\alpha)] = \ln A - E/(RT) \quad (1)$$

and Coats-Redfern's equation [5]

$$\ln[g(\alpha)/T^2] = \ln(AR)/(\beta E) - E/(RT) \quad (2)$$

were applied to the TG and DTG curves to analyse steps 1, 2 and 3.

In the above equations, α is the fraction of the reacted material; T is the absolute temperature, $f(\alpha)$ and $g(\alpha)$ are differential and integral mechanism functions, respectively. E and A are the derived apparent activation energy and pre-exponential factor, respectively. R is the gas constant and β is the heating rate.

Table 3 Data for step 1 of the decomposition of $[Cu(NBOCTB)][Cu(NO_3)_4]\cdot H_2O$ obtained from the TG and DTG curves

No.	T_i/K	α_i	$(\mathrm{d}\alpha/\mathrm{d}t)_i/\mathrm{min}^{-1}$
1	391.2	0.2357	3.225
2	393.2	0.2786	3.491
3	394.2	0.3857	3.567
4	395.2	0.4857	3.681
5	396.2	0.5928	3.719
6	398.2	0.7143	3.643
7	399.2	0.7858	3.605
8	400.2	0.9000	3.567
9	401.2	0.9072	3.491

Table 4 Data for step 2 of the decomposition of $[Cu(NBOCTB)][Cu(NO_3)_4]\cdot H_2O$ obtained from the TG and DTG curves

No.	T_i/K	α_i	$(\mathrm{d}\alpha/\mathrm{d}t)_i/\mathrm{min}^{-1}$
1	471.2	0.1328	0.6500
2	472.2	0.1745	0.9286
3	474.2	0.2675	1.996
4	474.7	0.3137	2.786
5	475.2	0.3708	3.238
6	475.7	0.4394	3.413
7	476.2	0.5016	3.355
8	477.2	0.6241	2.670
9	477.7	0.6709	2.205
10	479.2	0.7646	0.6964

The possible forms of $f(\alpha)$ and $g(\alpha)$ are listed in Table 2. The original data for steps 1, 2 and 3 determined from the TG and DTG curves are listed in Tables 3, 4 and 5 respectively.

Table 5 Data for step 3 of the decomposition of $[Cu(NBOCTB)][Cu(NO_3)_4]\cdot H_2O$ obtained from the TG and DTG curves

No.	T_i/K	α_i	$(d\alpha/dt)_i$/min^{-1}
1	508.2	0.07404	0.9036
2	513.2	0.2138	1.807
3	515.2	0.2704	2.108
4	518.2	0.3827	2.450
5	522.2	0.5266	2.590
6	525.2	0.6165	2.390
7	527.2	0.6922	2.088
8	529.2	0.7654	1.908
9	531.2	0.8195	1.486
10	533.2	0.8844	0.9839

Using the possible forms of $f(\alpha)$ and $g(\alpha)$ in Table 2, the data in Tables 3, 4 and 5 are analyzed by use of Eqs (1) and (2). For Eqs (1) and (2), the kinetic analyses were completed by the linear least-squares method on a TI-59 computer. The results are shown in Tables 6 –8 respectively.

Table 6 Results of analysis of the data for step 1 in Table 3 using Achar's Eq. (1) and Coats-Redfern's Eq. (2)

	Coats-Redfern method			Achar method		
No.	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r
1	371.1	107.5	0.9783	196.3	56.78	0.9688
2	432.7	126.0	0.9846	314.6	92.44	0.9909
3	459.8	132.9	0.9867	367.3	107.2	0.9922
4	515.7	150.2	0.9892	466.1	137.5	0.9904
5	300.6	87.17	0.9914	303.5	90.39	0.9662
6	197.9	55.55	0.9910	201.2	58.96	0.9339
7	146.9	39.83	0.9910	150.0	43.18	0.8923
8	95.8	23.91	0.9906	98.8	27.26	0.7957
9	70.2	15.84	0.9902	73.2	19.22	0.6980
10	234.2	65.73	0.9875	155.5	44.22	0.9750
11	254.7	71.69	0.9894	204.9	58.96	0.9709
12	182.2	50.20	0.9775	7.4	–0.57	0.4759

Table 6 Continued

	Coats-Redfern method			Achar method		
No.	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r
13	87.9	21.14	0.9758	−87.1	−29.60	0.9864
14	478.4	142.1	0.9855	600.4	181.5	0.9606
15	141.5	38.77	0.9506	451.6	135.2	0.9626

Table 7 Results of analysis of the data for step 2 in Table 4 using Achar's Eq. (1) and Coats-Redfern's Eq. (2)

	Coats-Redfern method			Achar method		
No.	EkJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r
1	874.5	214.5	0.9889	587.6	144.9	0.7374
2	953.7	234.4	0.9913	752.1	179.3	0.8208
3	985.1	240.9	0.9920	779.1	191.6	0.8468
4	1003	245.7	0.9906	883.0	218.1	0.8862
5	570.3	138.6	0.9938	459.1	113.3	0.7631
6	377.5	89.65	0.9937	265.9	64.26	0.5656
7	281.2	65.08	0.9936	170.0	39.86	0.4035
8	184.8	40.40	0.9934	73.2	15.04	0.1884
9	136.7	27.96	0.9933	64.7	12.64	0.2453
10	496.8	119.0	0.9923	302.7	72.76	0.5678
11	477.2	113.7	0.9762	354.7	85.62	0.6416
12	432.7	103.2	0.9887	4.6	−2.19	0.6147
13	212.4	47.26	0.9883	−73.4	−22.25	0.1581
14	744.4	183.3	0.9916	770.3	192.7	0.9252
15	148.0	31.38	0.9417	614.5	152.3	0.7657

Table 8 Results of analysis of the data for step 3 in Table 5 using Achar's Eq. (1) and Coats-Redfern's Eq. (2)

	Coats-Redfern method			Achar method		
No.	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r
1	395.0	85.06	0.9553	206.4	43.86	0.7928
2	436.1	94.17	0.9674	281.2	60.82	0.8925
3	454.0	96.94	0.9669	328.8	70.40	0.9262
4	488.5	105.1	0.9774	372.0	80.70	0.9536
5	268.0	56.68	0.9851	183.0	39.54	0.9642
6	175.8	35.15	0.9846	90.7	18.04	0.9301

Table 8 Continued

	Coats-Redfern method			Achar method		
No.	E/kJ mol^{-1}	ln$A$/s^{-1}	r	E/kJ mol^{-1}	ln$A$/s^{-1}	r
7	129.7	24.31	0.9840	44.6	7.21	0.8384
8	83.6	13.32	0.9829	–1.5	–3.75	0.0674
9	60.5	7.72	0.9817	–24.6	–9.31	0.7746
10	227.1	46.17	0.9715	93.7	17.84	0.7826
11	239.9	48.84	0.9766	123.5	24.44	0.8810
12	193.2	38.71	0.9534	4.6	–2.47	0.0457
13	92.2	15.14	0.9492	–96.4	–25.98	0.8011
14	371.4	81.34	0.9959	361.2	81.54	0.9974
15	80.5	13.19	0.9503	272.0	59.86	0.9939

The results in Table 6 clearly show that the values of E and A obtained from the two equations are approximately the same and the correlation coefficients are better when the probable mechanism function is function No. 5 (in Table 2). We concluded that step 1 has a Coring and Growth mechanism ($n=1$), the non-isothermal kinetic equation being $d\alpha/dt=Ae^{-E/RT}(1-\alpha)$.

From Tables 7 and 8 with the same inference, we consider that steps 2 and 3 both have Two-order Chemical Reaction mechanisms (No. 14). The non-isothermal kinetic equation for steps 2 and 3 is $d\alpha/dt=Ae^{-E/RT}(1-\alpha)^2$.

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