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Studies on the synthesis and non-isothermal kinetics of thermal decomposition for the complex [Ba(dibenzo-24-crown-8)(H_2O)$_2$][Co(NCS)$_4$]

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Abstract

Crystals of the complex [Ba(dibenzo-24-crown-8)(H_2O)$_2$][Co(NCS)$_4$] were obtained by the gel method. Its thermal decomposition reaction was studied in a dynamic atmosphere of dry nitrogen using TG–DTG. The thermal decomposition processes of the complex were determined and their kinetics were investigated. The kinetic parameters were obtained from analysis of the TG–DTG curves by integral and differential methods. The most probable mechanism function was suggested by comparison of the kinetic parameters. Mathematical expressions for the kinetic compensation effect were derived. Some valuable results have also been obtained and are discussed.

INTRODUCTION

The macrocyclic polyether dibenzo-24-crown-8 (DB24C8) can form complexes with alkali metals and alkaline earth metal salts [1,2]. Studies on the complexes of barium picrate and barium perchlorate with DB24C8 have been carried out [3, 4]. In this paper, the synthesis, and the thermal decomposition processes and kinetics for the complex [Ba(dibenzo-24-crown-8)(H_2O)$_2$][Co(NCS)$_4$] are reported.

EXPERIMENTAL

Synthesis of the complex [Ba(dibenzo-24-crown-8)(H_2O)$_2$][Co(NCS)$_4$]

Tetraethylsilicate (C.P.), water and acetonitrile (A.R.) were mixed in the volume ratio 1:1:2. An appropriate amount of dibenzo-24-crown-8 (chromatographic standard) was added and dissolved to make the concentration of the crown ether 0.1 mol l^{-1}. The mixture was thickened by heating under reflux for about 1 h, and then poured into a graduated

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cylinder. After 24 h, a silico-organic gel column was formed. A mixed solution of hydrous cobaltous chloride (A.R. 0.1 mol l^{-1}) and barium thiocyanate (0.4 mol l^{-1}) was poured over the column and allowed to diffuse into it at room temperature. Blue crystals of the complex began to grow on the surface and inside the gel column after 1 week.

Analytical data for the complex $C_{28}H_{36}N_4O_{10}S_4BaCo$ were as follows: found (calcd.) (%) C, 36.50 (36.83); H, 4.02 (3.97); and N, 6.10 (6.14). Structural analysis showed that its molecular formation conforms to [Ba(dibenzo-24-crown-8)$(H_2O)_2$][Co$(NCS)_4$].

TG–DTG experimental equipment and conditions

Thermogravimetric measurements were performed on Perkin-Elmer model TGS-2 (USA) with a nitrogen flow rate of 20 ml min^{-1}, in the temperature range 40–800°C and with a linear heating rate of 10.00°C min^{-1}. The amount of sample used was about 4 mg.

RESULTS AND DISCUSSION

Thermal decomposition processes

The TG–DTG curves of the complex in the temperature range 40–800°C are shown in Fig. 1. They show that the thermal decomposition processes of the complex [Ba(dibenzo-24-crown-8)$(H_2O)_2$][Co$(NCS)_4$] involves three steps. The probable thermal decomposition steps of the complex are

$$\mathrm{BaCo(DB24C8)(NCS)_4 \cdot 2H_2O \xrightarrow{I} BaCo(DB24C8)(NCS)_4 \xrightarrow{II}}$$

$$\mathrm{BaCo(NCS)_4 \cdot 0.25(DB24C8) \xrightarrow{III} BaCo(NCS)_4}$$

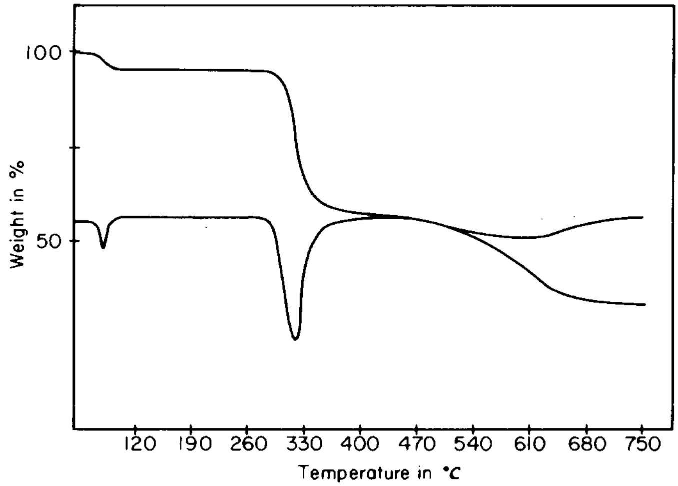

Fig. 1. TG–DTG curves of BaCo(DB24C8)$(NCS)_4 \cdot 2H_2O$.

TABLE 1

The thermal decomposition data of $BaCo(DB24C8)(NCS)_4 \cdot 2H_2O$ by TG–DTG

Steps	Temperature range°C		Mass loss in %	
	TG	DTG	Found	Calc.
I	68.0–93.5	68.3–80.4[a]–94.0	4.06	3.94
II	281.0–423.0	280.0–318.7[a]–367.5	37.78	38.40
III	465.0–691.1	465.0–590.0[a]–688.5	21.43	20.78

[a] Peak temperature for DTG curve.

The decomposition data corresponding to each of the three steps are given in Table 1.

The kinetics of the thermal decomposition reactions for the complex $BaCo(DB24C8)(NCS)_4 \cdot 2H_2O$

In this paper, the Narahari Achar et al. differential equation [5] and the Coats–Redfern integral equation [6] are used to analyse the kinetic problems for the thermal decomposition processes of the complex. The equations are

Coats–Redfern integral equation

$$\ln\frac{g(\alpha)}{T^2}=\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \tag{1}$$

Narahari Achar et al.'s differential equation

$$\ln\left[\frac{\mathrm{d}\alpha/\mathrm{d}T}{f(\alpha)}\right]=\ln\frac{A}{\beta}-\frac{E}{RT} \tag{2}$$

In the above equations, α is the fraction of the reacted materials, 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-exponental factor, respectively, R is the gas constant and β is the linear heating rate.

In order to obtain the kinetic information of the complex $BaCo(DB24C8)(NCS)_4 \cdot 2H_2O$, nineteen possible forms of $f(\alpha)$ and $g(\alpha)$ were selected and used to fit eqns. (1) and (2). The selected $f(\alpha)$ and $g(\alpha)$ forms are listed in Table 2.

Using the possible forms of $g(\alpha)$ and $f(\alpha)$, the data in Tables 3–5 are analysed using eqns. (1) and (2). The kinetic analyses were completed on an IBM computer. The T term in $\ln[AR(1-2RT/E)/\beta E]$ of eqn. (1) was assigned the value of the mean temperature of the original data. The data for kinetic analysis of the three decomposition steps are shown in Tables 3–5, and the results of the kinetic analysis are listed in Tables 6–8.

TABLE 2

The forms of $f(\alpha)$ and $g(\alpha)$ used for the analysis

Function no.	Function form	
	Integral form $g(\alpha)$	Differential form $f(\alpha)$
1	α^2	$1/2\alpha$
2	$\alpha + (1-\alpha)\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{-1}$
3	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	$1.5[(1-\alpha)^{-1/3}-1]^{-1}$
4	$[1-(1-\alpha)^{1/3}]^2$	$1{\cdot}5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3})]^{-1}$
5	$[(1+\alpha)^{1/3}-1]^2$	$1.5(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$
6	$[1/(1-\alpha)^{1/3}-1]^2$	$1.5(1-\alpha)^{4/3}[\{1/(1-\alpha)^{1/3}-1\}]^{-1}$
7	$-\ln(1-\alpha)$	$(1-\alpha)$
8	$[-\ln(1-\alpha)]^{2/3}$	$1.5(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
9	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[1-\ln(1-\alpha)]^{1/2}$
10	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
11	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
12	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
13	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$
14	α	1
15	$\alpha^{1/2}$	$2\alpha^{1/2}$
16	$\alpha^{1/3}$	$3\alpha^{2/3}$
17	$\alpha^{1/4}$	$4\alpha^{3/4}$
18	$(1-\alpha)^{-1}-1$	$(1-\alpha)^2$
19	$(1-\alpha)^{-1/2}$	$2(1-\alpha)^{3/2}$

TABLE 3

Data for step **I** of the thermal decomposition processes determined by TG–DTG

Data point	T_i/K	α_i	$(\mathrm{d}\alpha/\mathrm{d}T)_i$
1	347.65	0.1034	0.74
2	349.15	0.1576	1.17
3	350.65	0.2562	1.44
4	351.65	0.3227	1.57
5	352.65	0.4606	1.63
6	353.65	0.4606	1.72
7	354.65	0.5394	1.80
8	355.65	0.6182	1.71
9	357.15	0.7562	1.56
10	359.15	0.8645	0.87
11	361.15	0.9360	0.51

TABLE 4

Data for step **II** determined by TG–DTG

Data point	T_i/K	α_i	$(\mathrm{d}\alpha/\mathrm{d}T)_i$
1	577.15	0.09952	0.42
2	580.15	0.1533	0.54
3	583.15	0.2118	0.64
4	586.15	0.2843	0.77
5	588.15	0.3444	0.84
6	590.15	0.4674	0.86
7	592.15	0.4674	0.85
8	594.15	0.5283	0.84
9	596.15	0.5876	0.81
10	599.15	0.6739	0.75

TABLE 5

Data for step **III** determined by TG–DTG

Data point	T_i/K	α_i	$(d\alpha/dT)_i$
1	783.15	0.09613	0.0721
2	793.15	0.1330	0.0865
3	803.15	0.1671	0.1058
4	813.15	0.2133	0.1202
5	823.15	0.2636	0.1346
6	833.15	0.3248	0.1442
7	843.15	0.3812	0.1538
8	853.15	0.4470	0.1587
9	863.15	0.5194	0.1731
10	873.15	0.5922	0.1635
11	883.15	0.6631	0.1587
12	893.15	0.7331	0.1490
13	903.15	0.7993	0.1394
14	913.15	0.8563	0.1202
15	923.15	0.9029	0.0962

TABLE 6

Results of the kinetic analysis of step **I**

Function no.	Integral method			Differential method		
	$\ln A/s^{-1}$	E/kJ mol^{-1}	r	$\ln A/s^{-1}$	E/kJ mol^{-1}	r
1	107.98	333.58	0.9591	46.08	142.83	0.6909
2	121.72	375.04	0.9718	72.71	222.06	0.8659
3	126.52	393.22	0.9768	83.34	257.31	0.9114
4	139.54	430.69	0.9849	106.06	323.25	0.9598
5	93.84	299.55	0.9517	27.10	94.60	0.5432
6	185.21	562.51	0.9980	174.14	521.04	0.9977
7	78.17	143.05	0.9931	56.74	170.91	0.9772
8	49.74	160.07	0.9929	28.29	87.92	0.9504
9	35.44	118.59	0.9927	13.98	46.42	0.8809
10	21.01	77.03	0.992	−0.44	4.93	0.2237
11	13.73	56.33	0.9919	−7.74	−15.82	−0.6208
12	62.02	198.72	0.9788	21.97	72.00	0.7249
13	66.38	212.36	0.9844	32.92	104.97	0.8763
14	50.50	163.84	0.9577	−11.40	−26.97	−0.8223
15	21.39	79.94	0.9546	−40.49	−111.76	−0.8223
16	11.52	50.64	0.9512	−50.36	−140.05	−0.8957
17	6.53	36.52	0.9474	−55.38	−154.20	−0.9200
18	119.40	361.64	0.9980	124.88	368.71	0.9946
19	27.23	93.00	0.9411	90.11	269.81	0.9978

TABLE 7

Results of the kinetic analysis of step **II**

Function no.	Integral method			Differential method		
	$\ln A/\mathrm{s}^{-1}$	$E/\mathrm{kJ\ mol}^{-1}$	r	$\ln A/\mathrm{s}^{-1}$	$E/\mathrm{kJ\ mol}^{-1}$	r
1	93.14	487.62	0.9866	63.36	325.97	0.9573
2	99.94	523.20	0.9901	75.00	385.15	0.9760
3	101.26	536.60	0.9913	78.16	407.53	0.9811
4	106.96	563.73	0.9933	87.21	450.99	0.9881
5	82.38	447.20	0.9833	48.99	267.93	0.9359
6	125.21	650.68	0.9977	114.37	581.33	0.9977
7	55.30	298.10	0.9956	40.10	207.64	0.9911
8	34.22	195.41	0.9955	19.05	105.03	0.9838
9	23.59	144.15	0.9953	8.43	53.72	0.9628
10	12.86	92.83	0.9949	−2.32	2.41	0.2062
11	7.42	67.22	0.9946	−7.77	−23.34	−0.9190
12	48.02	266.99	0.9916	25.86	142.47	0.9572
13	49.73	277.02	0.9931	29.98	164.19	0.9743
14	42.74	238.88	0.9860	12.98	77.30	0.7975
15	17.21	114.51	0.9848	−12.56	−47.03	−0.7713
16	8.52	73.05	0.9834	−21.25	−88.47	−0.9391
17	4.14	52.46	0.9818	−25.68	−109.20	−0.9660
18	70.32	369.25	0.9996	67.79	337.99	0.9997
19	5.33	55.35	0.9630	53.01	272.82	0.9988

The results in Tables 6–8 show that the values from the two methods are approximately the same and the linear correlation coefficients are better when the probable mechanism functions are functions no. 18 for steps **I** and **II**, and no. 6 for step **III**. We conclude that the kinetic equations of the thermal decomposition for the complex are

Step **I** $$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{A}{\beta}\mathrm{e}^{-E/RT}(1-\alpha)^2$$

Step **II** $$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{A}{\beta}\mathrm{e}^{-E/RT}(1-\alpha)^2$$

Step **III** $$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{A}{\beta}\mathrm{e}^{-E/RT}1.5(1-\alpha)^{4/3}\{[1/(1-\alpha)^{1/3}-1]\}^{-1}$$

The calculated values of the kinetic parameters for the three steps are summarized in Table 9.

The kinetic compensation effect

According to the mathematical expression for the kinetic compensation effect, $\ln A = aE + b$, we fitted the kinetic parameters (E and $\ln A$) obtained from the integral method by the linear least-squares method. The obtained values of a and b are listed in Table 10.

TABLE 8

The results of the kinetic analysis of step **III**

Function no.	Integral method			Differential method		
	$\ln A/\mathrm{s}^{-1}$	$E/\mathrm{kJ\,mol}^{-1}$	r	$\ln A/\mathrm{s}^{-1}$	$E/\mathrm{kJ\,mol}^{-1}$	r
1	17.50	176.13	0.9843	10.99	111.75	0.9256
2	19.53	176.33	0.9914	15.85	148.44	0.9759
3	19.34	204.74	0.9936	16.67	163.87	0.9859
4	22.01	221.90	0.9969	21.80	193.10	0.9960
5	11.94	158.02	0.9799	4.77	85.95	0.8780
6	31.04	280.37	0.9994	34.30	280.79	0.9976
7	9.75	117.68	0.9992	11.03	104.31	0.9985
8	3.36	73.75	0.9981	4.61	60.37	0.9954
9	0.10	51.78	0.9989	1.31	38.40	0.9879
10	−3.43	29.82	0.9983	−2.10	16.43	0.9332
11	−4.34	18.82	0.9973	−3.89	5.45	0.6422
12	5.87	97.60	0.9937	3.72	60.47	0.9742
13	6.47	103.90	0.9963	5.52	75.05	0.9931
14	3.89	80.99	0.9817	−2.19	16.62	0.4785
15	−2.88	33.44	0.9725	−9.13	−30.94	−0.8027
16	−4.51	17.58	0.9552	−11.62	−46.80	0.9158
17	−7.71	9.65	0.9182	−15.16	−54.72	0.9431
18	17.74	168.68	0.9936	−22.03	191.98	0.9813
19	−3.10	28.71	0.8733	14.73	148.14	0.9902

TABLE 9

Calculated values of the kinetic parameters for the three decomposition steps

Steps	Integral method			Differential method		
	$E/\mathrm{kJ\,mol}^{-1}$	$\ln A/\mathrm{s}^{-1}$	r	$E/\mathrm{kJ\,mol}^{-1}$	$\ln A/\mathrm{s}^{-1}$	r
I	361.64	119.40	0.9980	368.71	124.88	0.9946
II	369.25	70.32	0.9996	337.99	67.79	0.9997
III	280.37	31.04	0.9994	280.79	34.30	0.9994

TABLE 10

Calculated values of the kinetic compensation parameters for the three decomposition steps

Step	a	b	r
I	0.338	−5.10	0.9998
II	0.201	−5.72	0.9998
III	0.135	−7.26	0.9962

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