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THERMAL DECOMPOSITION OF BARIUM(II) TETRAPHENYLBORATE

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Abstract

Barium(II) tetraphenylborate, $Ba(Bph_4)_2{\cdot}4H_2O$ was prepared, and its decomposition mechanism was studied by means of TG and DTA. The products of thermal decomposition were examined by means of gas chromatography and chemical methods. A kinetic analysis of the first stage of thermal decomposition was made on the basis of TG and DTG curves and kinetic parameters were obtained from an analysis of the TG and DTG curves using integral and differential methods. The most probable kinetic function was suggested by comparison of kinetic parameters. A mathematical expression was derived for the kinetic compensation effect.

Keywords: barium(II) tetraphenylborate, non-isothermal kinetics, thermal decomposition

Introduction

Sodium tetraphenylborate is widely used in inorganic analysis, organic analysis, modern electrochemical analysis, optical analysis, organic synthesis, catalysis, etc. Since $NaBph_4$ was synthesized by Witting and his coworker in 1951 [1], the characteristics of alkali metal tetraphenylborates have been widely studied. However, very little work is found in literatures concering alkaline earth tetraphenylborates, especially in respect of thermal analysis. Here, an alkaline earth metal tetraphenylborate was prepared and characterized. The thermal decomposition mechanism and kinetic parameters were studied under non-isothermal conditions, the Achar differential equation [2] and the Coats-Redfern integral equation [3] were used to analyze the non-isothermal decomposition process. The integral and differential equations are as follows:

$$\ln(g(\alpha)/T^2) = \ln(AR/\beta E) - E/RT \qquad (1)$$

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$$\ln[(d\alpha/dt)/f(\alpha)] = \ln A - E/RT \qquad (2)$$

In the above equations, α is the fractional decomposition, T the absolute temperature (K), $d\alpha/dt$ the reaction rate, A the preexponential Arrhenius factor, β the heating rate (K min^{-1}), E the apparent activation energy (kJ mol^{-1}), R the gas constant (kJ mol^{-1} K^{-1}), $f(\alpha)$ and $g(\alpha)$ the differential and integral functions, respectively.

Experimental

Purification of reagents and preparation of the compound

Analytical grade $NaBph_4$, $BaCl_2$ and cyclohexane were used as received. Ether (AR) was treated with $FeSO_4$ solution and distilled at 307.9 K ($n_D^{20}=1.2652$). Deionized water was redistilled (conductivity 1.22×10^{-4} Sm^{-1}).

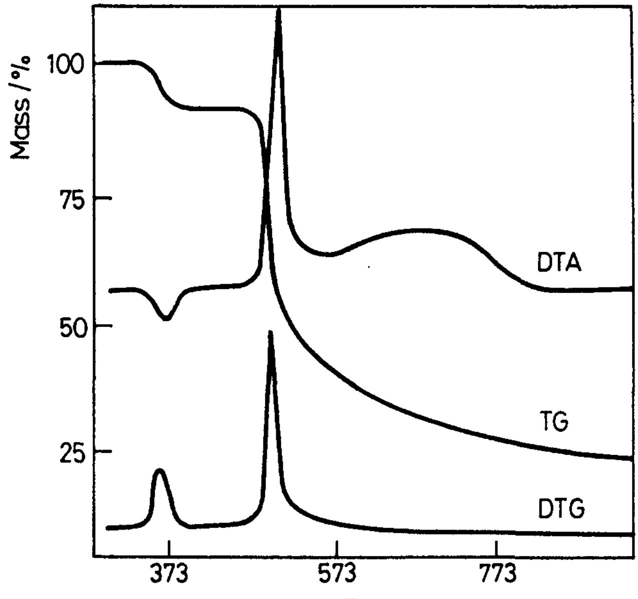

Fig. 1 TG, DTG and DTA curves of $Ba(Bph_4)_2\cdot4H_2O$

Preparation of barium tetraphenylborate. Prepare a solution of sodium tetraphenylborate by dissolving 2.15 g of the reagent in 35 ml of a mixture of ether and water (34.4:0.6 *v*/*v*), add this solution to 35 ml of 1.0 mol l^{-1} $BaCl_2$ solution in a separating funnel, shake it for 3 min, remove the aqueous phase, and mix the organic phase with another 35 ml portion of 1.0 mol l^{-1} $BaCl_2$ solution in the separating funnel just as above, and repeat twice. Distil the organic phase under a pressure of 40.52 kPa at 308 K until the ether is removed, change the pressure to 10.13 kPa and distil the residual solution to produce crystals of $Ba(Bph_4)_2\cdot 4H_2O$; wash the crystals three times with 10 ml portions of cyclohexane.

The product was purified as follows: the crystals were dissolved in water, the solution was filtered, then the filtrate was distilled at a pressure of 10.13 kPa at 308 K to yield crystals of $Ba(Bph_4)_2\cdot 4H_2O$. The crystals were dried at room temperature in a vacuum desiccator for 6 days before use. Analysis for $Ba(Bph_4)_2\cdot 4H_2O$ is as follows: C: 67.83 (68.04); H: 5.51 (5.71); B: 2.68 (2.55); Ba: 15.67 (16.19).

Physical measurement

Thermal analysis was carried out with an LCT-1 model TG-DTA instrument (Beijing Optical Instruments Factory, China). The working conditions were as

Table 1 Function forms used in the present analysis

Function No.	$f(\alpha)$	$g(\alpha)$
1	$1/(2\alpha)$	α^2
2	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$
3	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$	$(1-2/3\alpha)-(1-\alpha)^{1/3}$
4	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{2/3}]^2$
5	$3/2(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	$[(1+\alpha)^{1/3}-1]^2$
6	$3/2(1-\alpha)^{4/3}[\{1/(1-\alpha)^{1/3}-1\}]^{-1}$	$[\{1/(1-\alpha)\}^{1/3}-1]^2$
7	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
8	$(1-\alpha)$	$-\ln(1-\alpha)$
9–12	$(1/n)(1-\alpha)[-\ln(1-\alpha)]^{-(n-1)}$ $n = (2/3, 1/2, 1/3, 1/4)$	$[-\ln(1-\alpha)]^n$
13–14	$n(1-\alpha)^{(n-1)/n}$ $n = (2, 3)$	$1-(1-\alpha)^{1/n}$
15–18	$(1/n)\alpha^{-(n-1)}$ $n = (1, 1/2, 1/3, 1/4)$	α^n
19	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
20	$(1-\alpha)^{3/2}$	$(1-\alpha)^{-1/2}$
21–23	$(1/n)(1-\alpha)[-\ln(1-\alpha)]^{-(n-1)}$ $n = (2, 3, 4)$	$[-\ln(1-\alpha)]^n$
24	$1/2(1-\alpha)^3$	$[1/(1-\alpha)]^2-1$
25	$4(1-\alpha)^{3/4}$	$1-(1-\alpha)^{1/4}$
26	$6[1-(1-\alpha)^{1/3}]^{1/2}(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]^{1/2}$
27	$4[1-(1-\alpha)^{1/2}]^{1/2}(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]^{1/2}$
28–30	$(1/n)(1-\alpha)^{-(n-1)}$ $n = (2, 3, 4)$	$1-(1-\alpha)^n$

Table 2 Data for the dehydration process of $Ba(Bph_4)_2{\cdot}4H_2O$ determined on the basis of TG and DTG curves

No.	*T*/K	α	dα/d*t*
1	337.33	0.0589	0.1193
2	342.87	0.1397	0.2320
3	348.44	0.2506	0.3490
4	354.32	0.3715	0.5461
5	360.19	0.4923	0.6173
6	366.21	0.6060	0.5486
7	372.32	0.7097	0.4091
8	378.55	0.8134	0.2696
9	384.88	0.9172	0.1050

follows: rate of oxygen flow 60 ml min^{-1}, the measurement ranges 20 mg in TG, 250 μV in DTA and 5 mV min^{-1} in DTG, the heating rate was 5.00 K min^{-1}, the temperature range was 40 to 600°C, the sample mass was 12.44 mg. UV spectra were recorded with a Shimadzu 365 spectrometer. Gas chromatography was carried out with a HP5890 gas chromatograph.

Component analysis

Ba^{2+} and Bph_4^- were determined in barium tetraphenylborate according to the general procedure [4, 5] C and H contents were determined using a Perkin Elmer 240 elemental analyzer.

Results and discussion

Thermal decomposition process

The TG curves indicate that the earlier stage of thermal decomposition is a dehydration process with an endothermic DTA peak. Four water molecules were lost in one step for $Ba(Bph_4)_2{\cdot}4H_2O$ (mass loss: calcd. 8.50%, found 8.36%).

After the dehydration process, the organic material is oxidized until the level corresponding to barium borate $Ba(BO_2)_2$ is attained. This oxidative process involves two decomposition steps, a fast oxidative step with a sharp exothermic DTA peak, and a slow step with a flat exothermic DTA peak. Four phenyl groups were lost in the fast step (mass loss calcd. 41.09%; found 41.71%). The others were lost in the slow step (mass loss calcd. 73.68%; found 73.96%). In order to identify the gaseous products of the decomposition of $Ba(Bph_4)_2{\cdot}4H_2O$, the volume of the crucible was changed to 0.5 ml and the amount of sample to

150 mg, the other experimental conditions were unchanged. Only H_2O and CO_2 were found in the gas mixture by gas chromatography. The final oxidative decomposition products is $Ba(BO_2)_2$, as also confirmed by means of alizarin red S solution [6].

Table 3 Results of kinetic analysis of the decomposition of $Ba(Bph_4)_2{\cdot}4H_2O$

Function	Differential method			Integral method		
No.	ln*A*	*E*/kJ mol^{-1}	*r*	ln*A*	*E*/kJ mol^{-1}	*r*
1	18.11	58.70	0.6905	33.56	108.50	0.9405
2	24.71	79.37	0.8162	36.94	119.69	0.9546
3	26.32	88.24	0.8562	37.14	124.43	0.9600
4	32.21	104.96	0.9092	40.64	134.13	0.9692
5	10.80	44.56	0.5921	27.69	98.58	0.9305
6	39.56	125.86	0.9491	52.63	167.57	0.9877
7	8.760	30.08	0.4993	24.19	79.88	0.9383
8	16.93	51.62	0.8873	22.32	71.92	0.9783
9	8.05	25.64	0.7518	13.40	45.95	0.9762
10	3.53	12.66	0.5263	8.83	32.96	0.9739
11	-1.10	-0.32	0.0174	4.09	19.98	0.9684
12	-3.51	-6.81	0.3606	1.58	13.49	0.9609
13	7.42	26.54	0.6059	17.43	60.51	0.9590
14	9.95	34.90	0.7356	18.34	64.07	0.9662
15	-0.70	1.46	0.0339	14.69	51.25	0.9337
16	-10.46	-27.15	0.6196	4.80	22.63	0.9164
17	-13.89	-36.70	0.7573	1.23	13.09	0.8926
18	-15.69	-41.47	0.8074	-0.72	8.32	0.8570
19	34.58	101.77	0.9915	33.02	101.41	0.9934
20	25.07	76.69	0.9696	4.39	19.09	0.9128
21	43.05	129.53	0.9537	48.48	149.83	0.9800
22	68.88	207.44	0.9661	74.32	227.75	0.9806
23	94.59	285.36	0.9710	100.04	305.67	0.9808
24	52.92	151.93	0.9949	46.88	138.14	0.9882
25	13.91	39.08	0.7854	18.74	65.94	0.9696
26	-1.51	-0.12	0.0052	6.77	29.04	0.9569
27	-3.62	-6.71	0.2411	6.28	27.26	0.9497
28	-17.66	-48.69	0.6304	10.29	37.82	0.8751
29	-34.90	-98.85	0.7889	7.22	28.92	0.165
30	-52.26	-149.0	0.454	5.00	22.71	0.612

These results suggested a possible decomposition process of $Ba(Bph_4)_2{\cdot}4H_2O$ under O_2 as follows:

$$Ba(Bph_4)_2{\cdot}4H_2O \xrightarrow{328-423K} Ba(Bph_4)_2 \xrightarrow{423-508K} Ba(OBph_2)_2 \xrightarrow{508-873K} Ba(BO_2)_2$$

$$Ba(B(C_6H_5)_4)_2(c)+60O_2(g) \longrightarrow Ba(BO_2)_2(c)+48CO_2(g)+20H_2O(g)$$

Non-isothermal kinetic study of the dehydration process

The possible forms of $f(\alpha)$ and $g(\alpha)$ are listed in Table 1. The original data for the dehydration process of $Ba(Bph_4)_2{\cdot}4H_2O$ determined on the basis of TG and DTG curves are listed in Table 2.

Using the possible forms of $g(\alpha)$ and $f(\alpha)$ in Table 1, the data in Table 2 were analyzed by use of Eqs (1) and (2). For Eqs (1) and (2), the kinetic analysis was completed by the linear least-squares method on an IBM computer. The results are shown in Table 3.

The results in Table 3 clearly show that the values of E and A yielded by the two methods are approximately the same and the linear correlation coefficients are better when the probable function of the mechanism is taken as function no. 19 in Table 1. It can be concluded that the probable function of the mechanism of the dehydration process of $Ba(Bph_4)_2{\cdot}4H_2O$ is function no. 19 in Table 1. The kinetic equation of this process is

$$d\alpha/dt = A\exp(-E/RT)(1-\alpha)^2$$

The kinetic compensation effect according to the mathematical expression is $\ln A = aE+b$, the kinetic parameters (E and $\ln A$) being computed by the linear least-squares method on a computer, and the kinetic compensation parameters a and b are obtained. The mathematical expression for the kinetic compensation effect is

$$\ln A = 0.3240E - 0.3847 \quad r = 0.9942$$

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