Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 287-292

MECHANISM OF THERMAL DECOMPOSITION OF BARIUM BENZOATE

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Abstract

Barium benzoate was synthesized in a hydrothermal reaction. The complex was characterized by elemental analysis, IR spectroscopy and X-ray powder diffraction. It was monoclinic and had a layered structure. The mechanism of thermal decomposition of the barium benzoate was studied by using TG, DTA, IR and gas chromatography-mass spectrometry. In a nitrogen atmosphere, the barium benzoate decomposed to form $BaCO_3$ and organic compounds: mainly benzophenone, triphenylmethane, etc.

Keywords: barium benzoate, hydrothermal reaction, thermal decomposition

Introduction

Alkaline earth metal benzoates are stable compounds. Although the mechanism of thermal decomposition of alkaline earth metal benzoates has been reported, virtually only the solid-phase products were studied, with little attention to the gas-phase products [1, 3]. We have carried out systematic research on the thermal decompositions of the benzoates. The process of thermal decomposition of alkaline earth metal benzoates was studied by using thermogravimetry (TG) and differential thermal analysis (DTA). The products of thermal decomposition of the alkaline earth metal benzoates were characterized by IR spectroscopy and gas chromatography-mass spectrometry. In this paper, the mechanism of thermal decomposition of barium benzoate is discussed.

Experimental

Preparation of samples

Barium carbonate, benzoic acid, anhydrous ethanol, diethyl ether and acetone were obtained from the Shang Hai Chemical Reagents Plant. These reagents and analytical grade solvents were used without further purification.

Barium carbonate and benzoic acid were thoroughly mixed at a molar ratio of 1:2 with a little water in a hydrothermal reactor, and allowed to react to form

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1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

$Ba(C_6H_5COO)_2$ at 100°C for 10 h. Subsequently, the sample formed was washed three times with anhydrous ethanol or diethyl ether and dried at 150°C for 4 h. Anhydrous barium benzoate was obtained.

Characterization of samples

The carbon and hydrogen contents were determined with a Perkin Elmer 240B element analyzer. The content of Ba was determined by titration with EDTA.

Infrared spectra were measured with a Nicolet 60SXB spectrophotometer. Readings were taken over the range 4000–400 cm^{-1}. The matrix material was KBr.

The process of thermal decomposition was studied by DTA and TG, using a Shimadzu model DT-40 instrument in nitrogen and air media, at a heating rate of 20°C min^{-1}. Platinum cups were used as sample and reference holders, and alumina as a reference material.

The X-ray diffractograms were taken on a Rigaku D/MAX-RA X-ray diffractometer, using a graphite monochromator and $CuK_{\alpha 1}$ radiation.

Collection and characterization of decomposition products

A sample of 5–10 g was decomposed in a nitrogen atmosphere in a tubular furnace at 550°C and the gas-phase products were collected [4]. The solid residue was collected from the thermal balance under N_2 at 550°C. The products were characterized by IR spectrophotometry and VG analytical 7070 E-HF gas chromatography-mass spectrometer.

Results and discussion

Elemental analyses

The barium benzoate gave the following results. Found: Ba 35.69, C 44.54, H 2.84%; Calc.: Ba 36.18, C 44.30, H 2.66%. The sample can be represented by the general formula $Ba(C_6H_5COO)_2$. The experimental data are in agreement with the calculated values.

IR spectrum

The IR spectrum of barium benzoate showed that the C–C stretching vibration bands are situated at 1589, 1490 and 1307 cm^{-1}. The OCO band lies at 1512 cm^{-1} for the anti-symmetric vibration and at 1420 cm^{-1} for the symmetric vibration. The difference between the $\nu_{as}(OCO)$ and $\nu_s(OCO)$ vibrations of the carboxyl group was 92 cm^{-1}, which showed that the carboxyl group is coordinated to the Ba atom in a bridging bidentate coordination mode [5, 7].

XRD data

The $Ba(C_6H_5COO)_2$ cell parameters were calculated from the XRD data. It is monoclinic: a=1.5381 nm, b=1.3743 nm, c=0.4510 nm, β=101.55°, V=0.9339 nm^3,

Z=3, D_x=2.025 g cm^{-3}. All lines of the X-ray powder diffraction pattern were indexed by using these crystal parameters. The calculated values are in accord with the experimental data. From the diffraction intensity data, the crystal structure of $Ba(C_6H_5COO)_2$ is a layered structure.

Thermal analyses

TG curves of barium benzoate in air and nitrogen atmospheres are shown in Fig. 1. It can be seen that the final solid product of thermal decomposition of barium benzoate in air and nitrogen atmospheres is $BaCO_3$. The loss in mass is 47.42 and 47.96%, respectively, in good agreement with the calculated value (48.01%). From Fig. 1(a), the thermal decomposition of barium benzoate in air atmosphere is seen to proceed in two stages. First, it decomposes to form $BaCO_3$ and C; the residue is black. The C is then lost due to oxidation when the sample is heated to 756°C, and white $BaCO_3$ is obtained. The C obtained in the first step is due to dehydrogenation of the phenyl radical. From Fig. 1(b), the thermal decomposition of barium benzoate in nitrogen atmosphere is observed to be basically complete at 555°C.

DTA curves of barium benzoate in air and nitrogen atmospheres are shown in Fig. 2. The curves exhibit two peaks: one fusion peak and one decomposition peak. In nitrogen atmosphere, the fusion and decomposition peaks are both endothermic. In air atmosphere, the fusion peak is endothermic, and the decomposition peak is a very sharp exothermic peak, due to the oxidation of the organic products of the thermal decomposition.

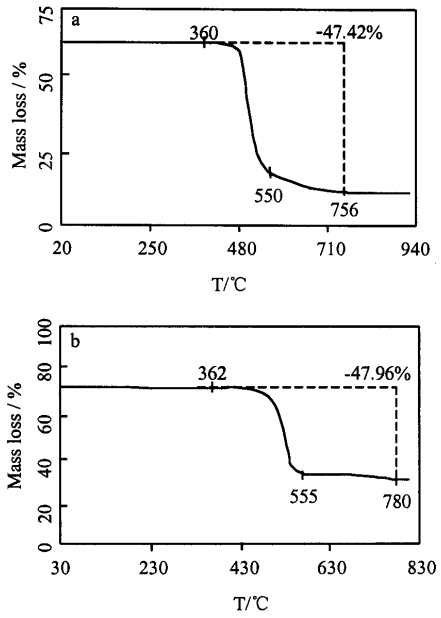


Fig. 1 TG curves of barium benzoate in air (a) and nitrogen (b)

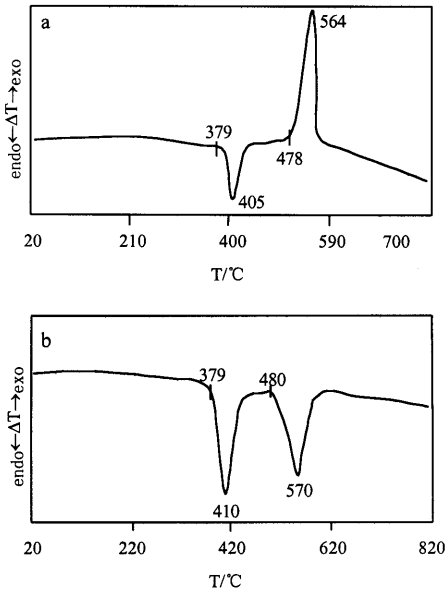


Fig. 2 DTA curves of barium benzoate in air (a) and nitrogen (b)

Collection and characterization of decomposition products

The solid product of thermal decomposition of barium benzoate at 550°C in nitrogen atmosphere is a grey powder. Its IR spectrum is depicted in Fig. 3. The absorption bands at 1418, 859 and 692 cm^{-1} are in agreement with the standard IR spectrum of $BaCO_3$ (Sadtler Standard Spectra, Y23S).

The observed and calculated TG data and the above IR data indicate that the final solid-phase product of thermal decomposition of barium benzoate in nitrogen and air atmospheres is $BaCO_3$.

The condensate of the gas-phase products of the thermal decomposition of barium benzoate at 550°C in nitrogen atmosphere is an orange sticky material. Its IR

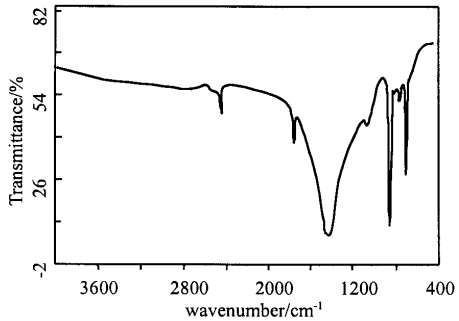


Fig. 3 IR spectrum of solid product of thermal decomposition of barium benzoate at 550°C in nitrogen atmosphere

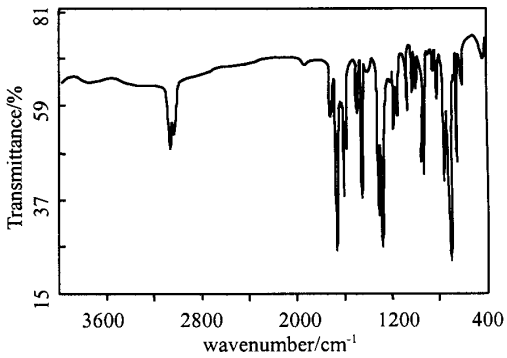


Fig. 4 IR spectrum of condensed gas-phase products of thermal decomposition of barium benzoate at 450°C in nitrogen atmosphere

Table 1 Combined results of gas chromatography and mass spectrography on barium benzoate

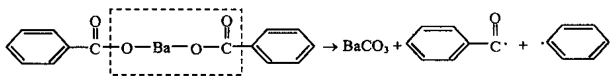
No.	Hold time/min	Content/%	Mol. mass	Product
1	18.564	9.72	154	biphenyl
2	19.56	4.06	168	diphenylmethane
3	23.32	43.04	182	benzophenone
4	25.91	11.50	180	fluorene
5	28.94	24.95	244	triphenylmethane
6	30.82	4.27	242	9-fluorenone

spectrum is presented in Fig. 4. The absorption peaks at 3059, 3027, 1599, 1447, 1316, 1152, 1074, 1028, 919, 848, 762, 739, 700 and 605 cm^{-1} are in accordance with the standard IR spectrum of triphenylmethane (Sadtler Standard Spectra, 18064K). The absorption peaks at 1659, 1576, 1278, 1176, 1000, 942, 809 and 638 cm^{-1} are in agreement with the standard IR spectrum of benzophenone (Sadtler Standard Spectra, 326K). The combined results of gas chromatography and mass spectrography are listed in Table 1: besides benzophenone and triphenylmethane, biphenyl, diphenylmethane, fluorene, 9-fluorenone, etc. were identified (mainly benzophenone and triphenylmethane).

Mechanism of thermal decomposition

The mechanism of thermal decomposition of barium benzoate is presented below:

The free radicals obtained in the thermal decomposition of barium benzoate take part in dehydrogenation reactions to form new free radicals and carbon:



(1)

$$C_6H_5CO\cdot \rightarrow \cdot C_6H_4CO\cdot + H \quad (2)$$

$$C_6H_5\cdot \rightarrow \cdot C_6H_4\cdot + H \quad (3)$$

$$\cdot C_6H_4\cdot \rightarrow 6C + 4H \quad (4)$$

The free radicals combine with each other to form benzophenone:

$$C_6H_5\cdot + C_6H_5CO\cdot \rightarrow C_6H_5COC_6H_5 \quad (5)$$

Benzophenone combines with H and $C_6H_5\cdot$ to form triphenylmethane:

$$C_6H_5COC_6H_5 + C_6H_5\cdot + 3H \rightarrow (C_6H_5)_3CH + H_2O \quad (6)$$

It can also participate in reactions to form biphenyl, fluorene, diphenylmethane, 9-fluorenone, etc.:

$$C_6H_5\cdot + C_6H_5\cdot \rightarrow C_6H_5C_6H_5 \quad (7)$$

$$\cdot C_6H_4\cdot + \cdot C_6H_4CO\cdot \rightarrow C_6H_4COC_6H_4 \quad (8)$$

$$(C_6H_5)_2CO + 4H \rightarrow C_6H_5CH_2C_6H_5 + H_2O \quad (9)$$

$$(C_6H_4)_2CO + C_6H_5\cdot + 3H \rightarrow (C_6H_4)_2CHC_6H_5 + H_2O \quad (10)$$

Conclusions

Barium benzoate can be synthesized in a hydrothermal reaction. It is monoclinic and has a layered structure.

The thermal decomposition of barium benzoate in air atmosphere proceeds in two stages: it first decomposes to form $BaCO_3$, C and CO; the C is then lost due to oxidation, and white $BaCO_3$ is obtained.

Barium benzoate decomposes in nitrogen atmosphere to form $BaCO_3$ and organic compounds, mainly benzophenone, triphenylmethane, etc.

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This work was supported by The National Natural Science Foundation of China (No. 29671025).

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