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Synthesis and thermal decomposition of zinc phthalate

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Abstract

Zinc phthalate was synthesized by the rheological phase reaction method, and the crystal structure was determined. Its thermal decomposition in argon was investigated. The thermal decomposition products were characterized by IR, XRD and GC–MS methods. Benzophenone, anthraquinone and nanoscale zinc oxide were chiefly obtained when zinc phthalate was pyrolyzed at 400–450°C in argon atmosphere. The free radical reaction mechanism of zinc phthalate in the thermal decomposition process was proposed. Fresh nanoscale ZnO plays a role as catalyst for the forming of benzophenone and anthraquinone.

Keywords: Crystal structure; Phthalate; Rheological phase reaction; Thermal decomposition; Zinc

1. Introduction

The thermal behaviour of transition metal and rare earth phthalates in air has been reported [1–5]. Brzyska et al. [6] have investigated the thermal decomposition of zinc phthalate hydrate in air. The thermal decomposition of the zinc phthalate hydrate proceeded in two stages. In the first step crystal water was lost to yield anhydrous salt, then the anhydrous salt was decomposed to zinc oxide in the second step. However, no other detailed study has been reported on the thermal decomposition reaction mechanism of zinc phthalate in inert atmosphere. In our previous works, xanthenone and dibenzofuran were obtained by thermal decomposition of zinc monosalicylate in argon. From the point of view of structure and component, $ZnC_6H_4(CO_2)_2$ can be pyrolyzed accompanying a decarboxylation to form the free radical $\cdot C_6H_4(CO)\cdot$ and to assemble to anthraquinone.

In this paper, zinc phthalate was synthesized by the rheological phase reaction method. The thermal decomposition reaction mechanism is investigated in inert atmosphere. The products of thermal decomposition are characterized. It is expected to obtain a new path of synthesizing anthraquinone.

The rheological phase reaction method is a process of preparing compounds or materials from a solid–liquid rheological mixture. The solid reactants were fully mixed in the proper molar ratio, and made up by adding a proper amount of water or other solvents to a solid–liquid rheological body in which the solid particles and liquid substance were uniformly distributed. After reaction under suitable experimental conditions the product was obtained. There are many advantages in the rheological phase system: the surface area of solid particle can be efficiently utilized, the contact between solid particle and fluid is close and uniform, heat exchange is very good, local overheating can be avoided, and the reaction temperature is easy to control. In addition, many substances exhibit new reaction properties in this state.

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2. Experimental

Preparation of samples: The phthalic acid and zinc oxide are of analytical reagent grade. The phthalic acid and zinc oxide were fully mixed by grinding in 1 : 1 molar ratio, a proper amount of water was added, and prepared to the solid–liquid rheological state (semisolid state). Then the mixture was reacted for 2 h at 80–90°C. Anhydrous zinc phthalate, ZnPht [Pht = $C_6H_4(CO_2)_2$], was obtained by drying at 120°C.

The contents of C, H and Zn were determined with a Perkin-Elmer 240B analyzer and by the use of EDTA titration, respectively. Elemental analysis found (calculated): Zn 28.40 (28.49), C 41.96 (41.87), H 1.65 (1.76) %.

The infrared spectra of the samples in KBr pellets were measured on a Nicolet 550 FT-IR spectrometer in the range 4000–400 cm^{-1}. The X-ray diffraction patterns were obtained with a Rigaku D/MAX-RA model X-ray diffractometer with a Ni-filter and graphite monochromator, and Cu K_{α_1} radiation ($\lambda = 0.15405$ nm). The TG and DTA (5.1–9.8 mg sample) curves of ZnPht were recorded with a Shimadzu DT-40 thermal analyzer in argon (flow rate 40 ml min^{-1}) at a heating rate of 20°C min^{-1} from room temperature to 900°C.

The collection of pyrolysis products: The sample (2 g) was pyrolyzed by employing the apparatus shown in the literature [7] in argon (flow rate 100 ml min^{-1}) at 450°C for 7 h, and the condensate of gas phase products was collected. Carbon dioxide was determined with $Ca(OH)_2$ solution.

The GC–MS analysis was carried out with a VG 7070E-HF gas chromatography–mass spectrometer (GC–MS), Beijing KYKY GC/MS-DS2 computer data system, HP 5790A gas chromatograph and OV1701 elastic quartz capillary column (0.32 mm in inside diameter and 30 m in length). Gas chromatography: the carrier gas was He, pre-column pressure 880 kPa, starting temperature 80°C, heating rate 8°C min^{-1}, final temperature 280°C, gasification temperature 290°C. Mass spectrometry: ionization manner was EI, ion source temperature 200°C, accelerating voltage 6 kV, electron energy 70 eV, scanning range 45–800 *m/z*.

3. Results and discussion

The powder X-ray diffraction data of ZnPht are listed in Table 1. The result indicated that the crystal structure of ZnPht is monoclinic, the calculated lattice parameters are $a = 1.1048 \pm 0.0001$, $b = 2.0057 \pm$

Table 1
Powder X-ray diffraction data of ZnPht[a]

2θ (deg)	d_{expt} (nm)	I/I_1	d_{calc} (nm)	h	k	l	2θ (deg)	d_{expt} (nm)	I/I_1	d_{calc} (nm)	h	k	l
8.02	1.1014	100	1.1011	1	0	0	23.35	0.3806	1	0.3804	2	3	1
8.80	1.0040	20	1.0029	0	2	0	23.75	0.3743	1	0.3728	2	1	$\bar{2}$
9.12	0.9688	33	0.9688	0	0	1	24.25	0.3667	5	0.3670	3	0	0
			0.9652	1	1	0	26.35	0.3379	1	0.3379	1	4	$\bar{2}$
12.55	0.7047	1	0.7098	1	1	$\bar{1}$	26.80	0.3324	1	0.3329	3	2	$\bar{1}$
			0.6994	1	0	1	27.60	0.3229	< 1	0.3229	0	0	3
13.25	0.6676	3	0.6686	0	3	0	28.45	0.3135	2	0.3131	1	1	$\bar{3}$
16.10	0.5500	1	0.5505	2	0	0	29.20	0.3056	< 1	0.3059	1	6	$\bar{1}$
			0.5503	0	3	1				0.3048	3	0	$\bar{2}$
16.60	0.5336	1	0.5309	2	1	0	32.45	0.2757	< 1	0.2757	2	5	$\bar{2}$
17.65	0.5021	< 1	0.5017	1	3	$\bar{1}$				0.2753	4	0	0
18.30	0.4844	6	0.4844	0	0	2	35.82	0.2505	1	0.2507	0	8	0
18.85	0.4704	11	0.4708	0	1	2				0.2504	2	4	$\bar{3}$
19.25	0.4607	< 1	0.4626	2	0	1	38.35	0.2345	< 1	0.2345	2	5	$\bar{3}$
20.70	0.4287	2	0.4305	1	0	2	39.80	0.2263	1	0.2265	1	3	$\bar{4}$
21.40	0.4149	2	0.4162	1	2	$\bar{2}$				0.2259	3	7	0
21.75	0.4083	2	0.4075	1	4	1							

[a] Monoclinic: $a = 1.1048$, $b = 2.0057$, $c = 0.9720$ nm, $\beta = 94.71°$, $V = 2.1467$ nm^3.

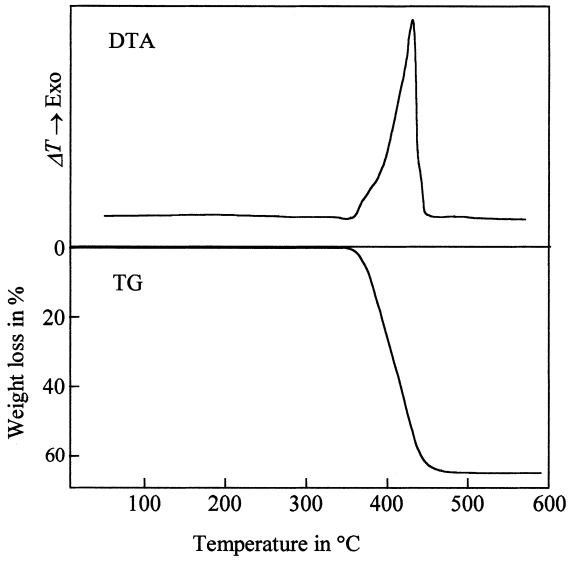


Fig. 1. TG and DTA curves of ZnPht in air.

0.0001, $c = 0.9720 \pm 0.0001$ nm, $\beta = 94.71 \pm 0.01^{\circ}$, $V = 2.1467$ nm^3. The intensity of strongest diffraction peak in (100) plane (Table 1) is about three times that of the second strongest peak. It indicates that the structure of zinc phthalate is layered, zinc ions located in the (100) plane and the benzene ring is situated on two sides of the zinc ion plane.

Figs. 1 and 2 show the TG and DTA curves of ZnPht in air and argon. ZnPht is stable below 340°C in air. On the DTA curve, a strong exothermic peak is observed at 433°C, which shows that decomposition and oxidation reaction of ZnPht occurred in air. The mass loss

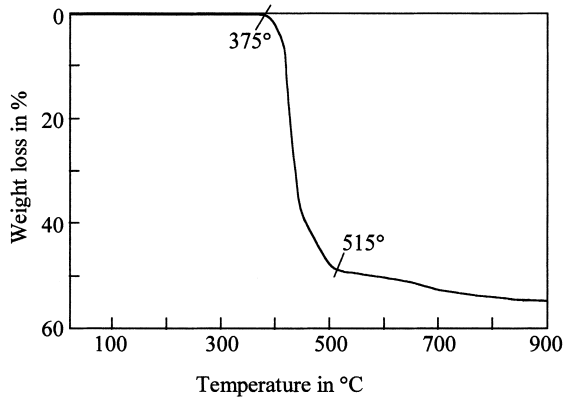


Fig. 2. TG curve of ZnPht in argon.

(64.12%) at 470°C agreed with a calculated value (64.54%) according to

$$ZnC_8H_4O_4 + 7.5O_2 = ZnO + 8CO_2 + 2H_2O \quad (1)$$

In argon atmosphere, ZnPht was decomposed rapidly at 375°C. The mass loss is 48.85% at 375–515°C, the solid residue was a black powder of zinc oxide and carbon.

When ZnPht was decomposed at 450°C in argon, CO_2 was detected in the gas products by means of a chemical method. The condensate of the gas phase products is dark brown and sticky oily matter. The results of GC–MS analysis are presented in Table 2. The main products were benzophenone and anthraquinone. In addition, small amounts of diphenyl, diphenylmethane, fluorene, fluorenone, triphenylmethane and 9-phenyl fluorene had been detected. The infrared spectrum (Fig. 3) of light yellow crystals separated from the condensate of the gas phase is consistent with the standard IR spectrum of anthraquinone (Sadtler No. 297 K).

The powder X-ray diffraction data of the solid residues are listed in Table 3. The reflections are in agreement with zinc oxide of hexagonal wurtzite structure (JCPDS card 5-0664). The lattice parameters were slightly enlarged, with values of $a = 0.325$, $c = 0.523$ nm and $V = 0.0478$ nm^3. By calculating with line-width method, the particle size of zinc oxide is about 5–10 nm.

The above results revealed the thermal decomposition mechanism as follows:

During the thermal decomposition of zinc phthalate, the fracture of bonds occurred chiefly in accordance with Eqs. (2) and (3), to form the free radicals $\cdot C_6H_4C(O)\cdot$ and $:C_6H_4$. Two $\cdot C_6H_4C(O)\cdot$ were reacted to anthraquinone (see Eq. (4)).

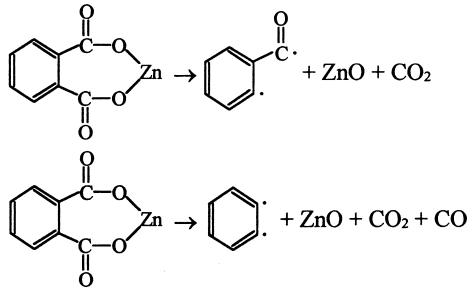


Table 2
GC–MS results of condensate of gas phase products for the thermal decomposition of ZnPht at 450°C in argon

No.	Retention time (min)	Molecular weight	Compound	Peak area (%)
1	14.525	154	Diphenyl	1.6
2	15.410	168	Diphenylmethane	1.5
3	18.039	166	Fluorene	0.4
4	18.758	182	Benzophenone	40.5
5	20.363	180	Fluorenone	0.6
7	23.558	208	9,10-Anthraquinone	48.2
8	23.932	244	Triphenylmethane	2.4
9	25.592	242	9-Phenylfluorene	4.8

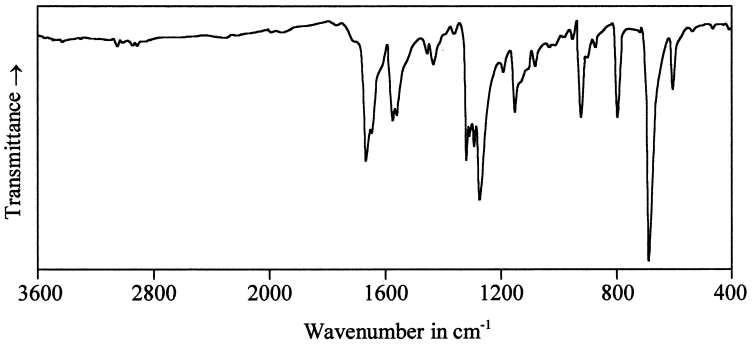
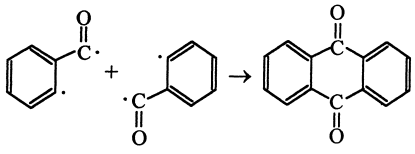


Fig. 3. The IR spectrum of thermal decomposition product (9,10-anthraquanone) of ZnPht at 450°C in argon.

Table 3
The powder X-ray diffraction data of ZnO from thermal decomposition of ZnPht at 450°C in argon[a]

2θ (deg)	d_{expt} (nm)	I/I_1	Half-peak breadth (deg)	d_{calc} (nm)	h	k	l	Grain size ($\perp hkl$) (nm)
31.70	0.2820	83	1.0	0.2815	1	0	0	9.2
34.20	0.2620	100	1.8	0.2615	0	0	2	5.1
36.15	0.2483	92	1.3	0.2478	1	0	1	7.1
47.40	0.1916	9	1.4	0.1916	1	0	2	6.9
56.60	0.1625	47	1.0	0.1625	1	1	0	10.0
62.70	0.1480	11	1.4	0.1482	1	0	3	7.4
67.90	0.1379	30	1.4	0.138	1	1	2	7.6

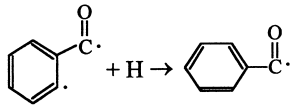
[a] Hexagonal: $a = 0.325$, $c = 0.523$ nm.



(4)

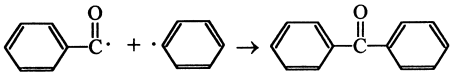
A part of $:C_6H_4$ was dehydrogenated easily to elemental C (Eq. (5)). At the same time, the $\cdot C_6H_4C(O)\cdot$ and $:C_6H_4$ were hydrogenated according to Eqs. (6) and (7), to produce $C_6H_5C(O)\cdot$ and $\cdot C_6H_5$, and then benzophenone was obtained by Eq. (8).

$$:C_6H_4 \rightarrow 6C + 4H \quad (5)$$



(6)

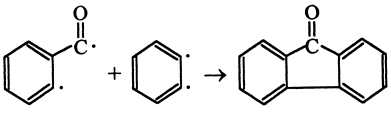
$$:C_6H_4 + H \rightarrow \cdot C_6H_5 \quad (7)$$



(8)

The presence of diphenyl and fluorenone in the products proved further the formations of free radicals described above.

$$2 \cdot C_6H_5 \rightarrow C_6H_5C_6H_5 \quad (9)$$



(10)

Diphenylmethane, fluorene, triphenylmethane and 9-phenylfluorene were results of the reaction of benzophenone and fluorenone with H and $\cdot C_6H_5$. The amount of these compounds is very small. This fact suggests that free radicals did not enter the gas phase, the reactions forming anthraquinone and benzophenone proceeded on the surface of solid products. Fresh nanoscale ZnO possesses probably very high catalytic activity for the formation of anthraquinone and benzophenone. If the condition of thermal decomposition reaction can be exactly controlled, the formations of by-products can be avoided.

Acknowledgements

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