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Study of the thermal degradation of benzene-containing glycerol carbonate derivatives by a combined TG–FTIR and theoretical calculation

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ABSTRACT

We recently found that the introduction of benzene ring as connection block improved the thermal stability of glycerol carbonate derivatives. To further explore how polysubstitution on benzene influences their thermal stability, another two derivatives, benzene-1,3,5-tricarboxylic acid tris-(2-oxo-[1,3]dioxolan-4-ylmethyl) ester (BATE1) and benzene-1,2,4,5-tetracarboxylic acid tetrakis-(2-oxo-[1,3]dioxolan-4-ylmethyl) ester (BATE2), were synthesized and characterized by a combined TG–FTIR and theoretical calculation. TG results showed that both BATE1 and BATE2 had three weight loss stages. FTIR spectra of evolved gases and the bond dissociation energy for the two compounds indicated that during the pyrolysis process, the C—C, C—O bonds of five-membered cyclic carbonate fractured preferentially to produce volatile carbonates and CO_2, and then the nearby C—O bond of esters continued to crack to produce more fragments. Finally, benzene ring still remains in the solid pyrolysis products. Therefore, improving the thermal stability of compound cannot be achieved simply by increasing the number of substituents on the benzene ring.

1. Introduction

As a representative of high-energy green batteries, lithium-ion batteries have many outstanding advantages like high voltage, high energy density, long cycle-life, low self-discharge and environment-friendly, but they still have some issues in durability, operating temperature and safety to improve [1–4]. Among these, the safety problems become a serious obstacle to wide application like plug-in electric vehicles and stand-by power sources for communications and modern airplanes [5,6]. The use of flammable organic electrolytes has been considered one of the primary reasons causing safety problems [7–9]. Therefore, more and more researchers have investigated the flammability and thermal stability of the electrolyte at higher temperature. TG–FTIR technique, having the advantages of minimal material requirement, simple temperature program control, and online recording, has been widely used to analyze thermal pyrolysis of compounds [10–13].

In our recent work [14], the investigation of thermal pyrolysis of three glycerol carbonate (GC) derivatives: carbonic acid bis-(2-oxo-[1,3]dioxolan-4-ylmethyl) ester (CABE), succinic acid bis-(2-oxo-[1,3] dioxolan-4-ylmethyl) ester (SABE) and terephthalic acid bis-(2-oxo-[1,3]dioxolan-4-ylmethyl) ester (TABE) by TG–FTIR showed us an interesting result that the 5% weight loss temperature was increased in the order of TABE > SABE > CABE, which means that the thermal stability of TABE is the best. Furthermore, it revealed that benzene ring was introduced as connection block to improve the thermal stability of the GC derivatives (e.g., greater than saturated hydrocarbon block). To further extend our previous work, it will be interesting to study how the number of substituents on the benzene ring affects the thermal stability. For example, whether improving the thermal stability can be simply obtained by introducing more substituents on benzene ring.

In this work, we increased the number of substituents on benzene in the molecular structure of terephthalic acid bis-(2-oxo-[1,3]dioxolan-4-ylmethyl) ester (TABE), designed and synthesized another two new GC derivatives: benzene-1,3,5-tricarboxylic acid tris-(2-oxo-[1,3]dioxolan-4-ylmethyl) ester (BATE1) and benzene-1,2,4,5-tetracarboxylic acid tetrakis-(2-oxo-[1,3]dioxolan-4-ylmethyl) ester (BATE2). The chemical structures of the two compounds are shown in Fig. 1. In order to understand how the substituents affect the thermal stability on this type of ester, TG–FTIR was used to explore the dynamic decomposition and analyze the gaseous products during the thermal pyrolysis of the two compounds. Furthermore, the theoretical calculations of the bond

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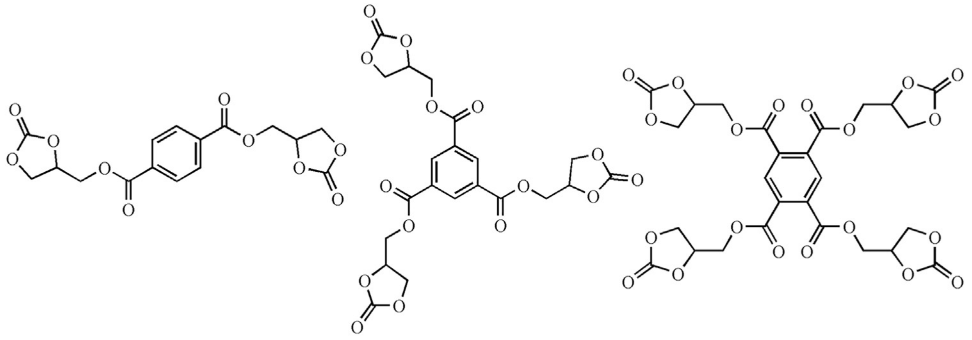

TABE **BATE1** **BATE2**

Fig. 1. Chemical structure of glycerol carbonate (GC) derivatives.

dissociation energy for both compounds were carried out for facilitating to clarify their thermal pyrolysis behaviors. This study may provide useful information for future molecular design and synthesis of new carbonates.

2. Experimental

2.1. Materials

Dimethyl carbonate (DMC, AR grade), calcium oxide (CaO, AR grade) and triethylamine (TEA, AR grade) were purchased from Tianjin Damao Chemical Reagent Factory (China). Glycerol (AR grade), thionyl chloride ($SOCl_2$, AR grade) and N,N-dimethylformamide (DMF, AR grade) were obtained from Tianjin Jiangtian Chemical Technology Co., Ltd. (China). Acetone (AR grade) was purchased from Tianjin No.1 Chemical Reagent Factory (China). Dichloromethane (AR grade) was obtained from Tianjin Fuqi Chemical Co., Ltd. (China). Trimesoyl chloride (98%) and pyromellitic dianhydride (99%) were purchased from Aladdin Reagent Co., Ltd. (China). CaO was calcined at 800 °C for 6 h before using; other chemicals were used as received without further purification.

2.2. Synthesis of glycerol carbonate (GC) derivatives

GC was synthesized by the transesterification of glycerol with DMC [14]. And pyromellitic acid chloride was synthesized from thionyl chloride and pyromellitic dianhydride. Then, GC was used as organic synthesis intermediate and further reacted with acid chloride to prepare GC derivatives.

2.2.1. Synthesis of benzene-1,3,5-tricarboxylic acid tris-(2-oxo-[1,3] dioxolan-4-ylmethyl) ester (BATE1)

In a dry 250 mL 3-necked round-bottomed glass flask equipped with a magnetic stirrer, a funnel with pressure-equalising tube and a thermometer was placed 4.13 g (0.035 mol) of glycerol carbonate, 4.16 mL (0.03 mol) of triethylamine and 60 mL of anhydrous acetone as solvent. A solution of trimesoyl chloride (2.65 g, 0.01 mol) in anhydrous acetone (40 mL) was added dropwise to the above solution cooled in ice bath under nitrogen atmosphere. The mixture was stirred at room temperature for 12 h. After reaction, triethylamine hydrochloride was removed by filtration. Then, the filtrate was evaporated under reduced pressure; the obtained residue was washed by deionized water for several times to give the product (3.83 g, yield 75.10%) (reaction 2, Scheme 1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.68 (s, 3H), 5.29–5.18 (m, 3H), 4.82–4.41 (m, 12H) (Fig. S1). FTIR (ν_{max} cm^{-1}): 2923, 1794, 1734, 1245, 1050, 738.

2.2.2. Synthesis of benzene-1,2,4,5-tetracarboxylic acid tetrakis-(2-oxo-[1,3]dioxolan-4-ylmethyl) ester (BATE2)

In a dry 250 mL 3-necked round-bottomed glass flask equipped with a magnetic stirrer, a funnel with pressure-equalising tube and a thermometer was placed 3.69 g (31.25 mmol) of glycerol carbonate, 3.47 mL (25 mmol) of triethylamine and 50 mL of anhydrous acetone as solvent. A solution of pyromellitic acid chloride (2.05 g, 6.25 mmol) in anhydrous acetone (30 mL) was added dropwise to the above solution cooled in ice bath under nitrogen atmosphere. The mixture was stirred at room temperature for 12 h. After reaction, triethylamine hydrochloride was removed by filtration. Then, the filtrate was evaporated under reduced pressure; the residue was purified by recrystallization from dichloromethane to give the product (1.04 g, yield 25.43%) (reaction 3, Scheme 1).

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.17 (s, 2H), 5.21–5.10 (m, 4H), 4.68–4.49 (m, 12H), 4.42–4.32 (m, 4H) (Fig. S2). FTIR (ν_{max} cm^{-1}): 2924, 1794, 1730, 1171, 1049, 768.

2.3. TG–FTIR measurement

The TG–FTIR system was composed of a TA SDT-600 Instrument and a Bruker Tensor 27 FTIR spectrometer. For each TG–FTIR measurement, 10–20 mg sample was weighted into an open alumina crucible. The temperature was set from ambient temperature to 600 °C, the heating rate of the TG furnace was 20 °C min^{-1}, and high purity ($>$ 99.999%) nitrogen gas with a flow rate of 140 mL min^{-1} was used as carrier gas, this flow had to be kept high enough to avoid long residence time in the furnace and thus to prevent secondary reactions of the volatiles [15]. The transfer line used to connect TG and FTIR was a 1 m long stainless steel tube with an internal diameter of 2 mm. In order to reduce the possibility of gases condensing along the transfer line, the temperature in the gas cell and transfer line were set to 200 °C. The FTIR spectral region was set as 4000–600 cm^{-1}, with the resolution of 4 cm^{-1}, co-adding 16 scans per spectrum. The experiment started only when the whole system was stable. The experimental results of TG and FTIR were recorded automatically by a computer. Data was processed by the software OPUS 6.0 (Bruker Company, Germany).

2.4. Bond dissociation energy (BDE) calculation

The quantum chemistry calculations were performed using the Gaussian 09 program. The molecular structures were optimized at the M062X/cc-pVTZ level of theory and frequencies and energies of the molecules were calculated at the same level of theory. All molecular structures without imaginary frequencies were local minima on the potential energy surfaces. Formula (1) described by Blanksby and Ellison [16], was used to calculate the bond dissociation energy (BDE) for a dissociation process: $R - Q \rightarrow R + Q$.

$$D_0(R - Q) = E_0(R) + E_0(Q) - E_0(R - Q) \qquad (1)$$

where $D_0(R - Q)$, $E_0(R)$, $E_0(Q)$ and $E_0(R - Q)$ denote to be the calculated BDE, and the electronic energies at 0 K with zero-point energy (ZPE) corrections for R, Q and R – Q, respectively.