

# The investigation of thermal pyrolysis of glycerol carbonate derivatives by TG–FTIR



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## ABSTRACT

Three new 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), were designed and synthesized. We investigated the thermal stability and the thermal pyrolysis of three compounds by TG–FTIR, and the bond dissociation energy was calculated to further demonstrate the decomposition process. The results showed that the three GC derivatives had one, two, three weight loss stages, respectively. Their initial decomposition temperature was as high as 200 °C, which means that the compounds have good thermal stability. 5% weight loss temperature was increased in the order of TABE > SABE > CABE. In thermal pyrolysis process, the C–C, C–O bonds of cyclic carbonate fractured preferentially, and then the C–O bonds nearby cyclic carbonate of SABE and TABE continued to fracture to produce linear ester in the form of fragment.

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## 1. Introduction

In spite of the successful introduction and increasing distribution of lithium-ion batteries in the world market, large-scale lithium-ion batteries with higher energy density are not yet commercially available for their practical application, such as electric vehicles, cellular phones, digital cameras and notebooks due to their associated safety problems [1–3]. With the scaling-up of lithium-ion batteries, the reduction of specific surface areas reduces the thermal dissipation rate. As heat accumulates in batteries, the thermal risk becomes much more serious than in normal batteries [4]. Therefore, in order to improve the safety performance of lithium-ion batteries, many researchers have investigated the flammability and thermal stability of the electrolyte at high temperature. The cyclic and linear carbonates are widely used for electrolytes of lithium-ion batteries. However, the linear carbonates have low flashing points and low boiling points, which is disadvantageous in terms of security [5]. By contrast, the cyclic carbonates have higher flashing points and boiling points, such as ethylene carbonate (EC), propylene carbonate (PC). Glycerol carbonate (GC) is a

rather new compound with many unique properties, such as high boiling point, high flash point, low flammability and low toxicity. Recently, it was reported that GC and its derivatives can be used as electrolytes in lithium-ion batteries instead of EC and PC [6,7]. Therefore, we designed and synthesized three new 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), which combined cyclic carbonate with various linear carbonate in order to have a better performance. Chemical structures of these compounds are shown in Fig. 1.

TG–FTIR technology is to transmit the escaping gas composition during the weight loss of sample in thermogravimeter to the infrared gas detection cell via constant temperature pipeline, through infrared detection, analysis and judgment the structure of escaping gas composition, proceeds quantitative and qualitative analysis, respectively. This method, which can conduct simultaneous and continuous real time analysis, is a useful technology for obtaining mass loss with time and evaluating the functional groups of the volatiles produced by pyrolysis [8–10]. This technique can give a deep insight into the evolution of pyrolysis and products information about the physical–chemical nature of the observed process. Therefore, it has been widely used in a variety of organic and inorganic materials in terms of thermal stability and thermal pyrolysis mechanism, even attracted more attention in the different research fields for different purposes [11–13].

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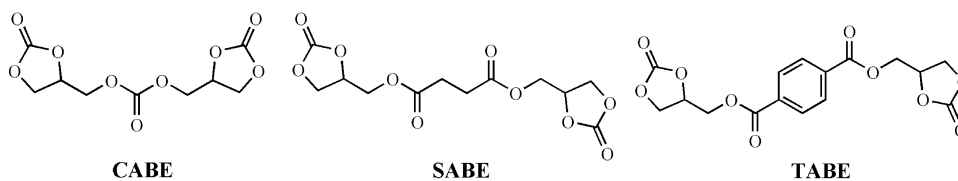


Fig. 1. Chemical structure of compounds.

In present work, three new glycerol carbonate derivatives were synthesized, and their thermal pyrolysis behaviors were studied by the TG–FTIR technique. Furthermore, the theoretical calculations of the bond dissociation energy for these compounds were carried out for clarifying their thermal behaviors. Our work is focused on investigation of the relationship between molecular structure and thermal stability of three GC derivatives (CBE, OBE and TBE) with TG–FTIR analysis and theoretical calculation. This study may provide the useful information for molecular design and synthesis of new carbonates.

## 2. Experimental

### 2.1. Synthesis of compounds

#### 2.1.1. Synthesis of glycerol carbonate (GC)

In a 250 mL 3-necked round-bottomed glass flask equipped with a magnetic stirrer, a reflux condenser and a thermometer was placed 36.84 g (0.40 mol) of glycerol, 118 mL (1.40 mol) of dimethyl carbonate and 1.35 g (0.024 mol) of CaO as a catalyst. The mixture was stirred at 75 °C and kept subsequently under reflux for 5 h. After reaction, the solid catalyst (CaO) was removed by filtration. Then, the methanol and the residue of dimethyl carbonate were distilled off at 45 °C under reduced pressure to give colorless liquid glycerol carbonate (42.13 g, yield 89.19%) (reaction 1, [Scheme 1](#)).

$^1\text{H}$  NMR (400 MHz, Acetone- $d_6$ ):  $\delta$  4.93–4.82(m, 1H), 4.58(t,  $J=8.4$  Hz, 1H), 4.49–4.35(m, 2H), 3.89(d,  $J=12.5$  Hz, 1H), 3.71(d,  $J=12.4$  Hz, 1H). FTIR ( $\nu_{\text{max}}$   $\text{cm}^{-1}$ ): 3402, 2931, 1784, 1186, 1084.

#### 2.1.2. Synthesis of carbonic acid

##### bis-(2-oxo-[1,3]dioxolan-4-ylmethyl) ester (CBE)

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 8.27 g (0.07 mol) of glycerol carbonate, 8.32 mL (0.06 mol) of triethylamine and 60 mL of anhydrous dichloromethane as solvent. A solution of bis(trichloromethyl) carbonate (2.97 g, 0.01 mol) in anhydrous dichloromethane (40 mL) was added dropwise to the above solution under nitrogen

atmosphere at 0 °C. The mixture was stirred at room temperature for 12 h. After reaction, the mixture was filtrated and the filtrate was evaporated under reduced pressure, the residues were purified by recrystallization from water to give the product (4.95 g, yield 63.05%) (reaction 2, [Scheme 1](#)).

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  5.12–5.01 (m, 2H), 4.58–4.25(m, 8H) (Fig. S1(a)). FTIR ( $\nu_{\text{max}}$   $\text{cm}^{-1}$ ): 2925, 1793, 1761, 1176, 1052.

Supplementary Fig. S1 related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tca.2015.12.002>.

#### 2.1.3. Synthesis of succinic acid

##### bis-(2-oxo-[1,3]dioxolan-4-ylmethyl) ester (SBE)

In a dry 100 mL 3-necked round-bottomed glass flask equipped with a magnetic stirrer, a funnel with pressure-equalising tube and a thermometer was placed 2.36 g (0.02 mol) of glycerol carbonate, 1.61 mL (0.02 mol) of pyridine and 30 mL of dry tetrahydrofuran as solvent. A solution of succinyl chloride (1.11 mL, 0.01 mol) in dry tetrahydrofuran (5 mL) was added dropwise to the above solution over 30 min under nitrogen atmosphere at –5 °C. The mixture was stirred for 4 h. After reaction, pyridine hydrochloride was removed by filtration. The filtrate was evaporated under reduced pressure, the residue was purified by recrystallization from acetone to give the product (1.00 g, yield 31.33%) (reaction 4, [Scheme 1](#)).

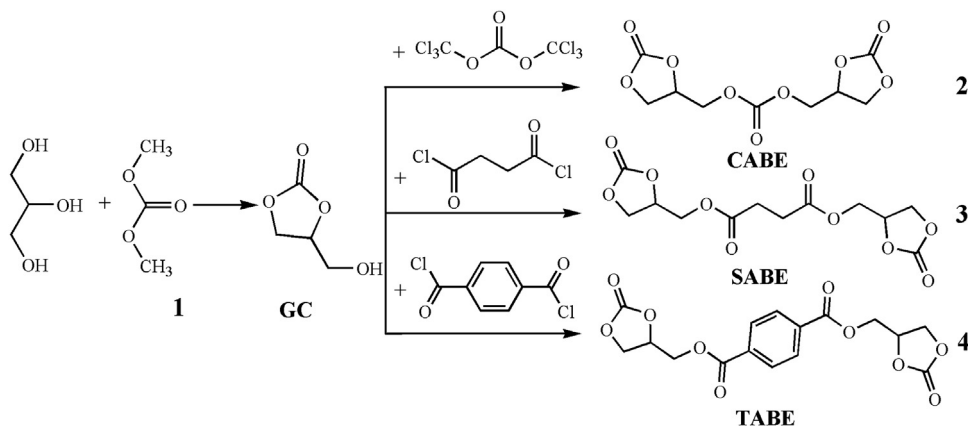
$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  5.08–4.99 (m, 2H), 4.57 (t,  $J=8.6$  Hz, 2H), 4.35–4.21 (m, 6H), 2.63 (s, 4H) (Fig. S1(b)). FTIR ( $\nu_{\text{max}}$   $\text{cm}^{-1}$ ): 2929, 1785, 1736, 1164, 1054.

Supplementary Fig. S1 related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tca.2015.12.002>.

#### 2.1.4. Synthesis of terephthalic acid

##### bis-(2-oxo-[1,3]dioxolan-4-ylmethyl) ester (TBE)

In a dry 100 mL 3-necked round-bottomed glass flask equipped with a magnetic stirrer, a funnel with pressure-equalising tube and a thermometer was placed 2.36 g (0.02 mol) of glycerol carbonate, 1.61 mL (0.02 mol) of pyridine and 30 mL dry tetrahydrofuran as solvent. A solution of terephthaloyl chloride (2.03 g, 0.01 mol) in dry tetrahydrofuran (15 mL) was added dropwise to the above



Scheme 1. The reaction route.

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