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**Review** article

# Studies on hydrolysis/alcoholysis/ammonolysis mechanisms of ethylene terephthalate dimer using DFT method

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#### ABSTRACT

Hydrolysis/alcoholysis/ammonolysis are considered as viable routes for efficient degradation and recycling of polyethylene terephthalate waste plastic. The possible hydrolysis/alcoholysis/ammonolysis pathways for the degradation of ethylene terephthalate dimer were investigated by the density functional theory (DFT) method M06/cc-pVDZ. The geometric structure optimization and frequency calculation of various intermediates, transition states and products involved in the reaction were carried out to obtain thermodynamic and kinetic parameter values. The results show that the reaction energy barrier of the cracking process of ethylene terephthalate dimer can be reduced under the conditions of hydrolysis/alcoholysis/ammonolysis, which makes the reaction easier. Additionally, at 298 K and 1 atm, the total rate constants of hydrolysis/alcoholysis/ammonolysis are  $1.51 \times 10^{-43}$  cm<sup>3</sup> molecular<sup>-1</sup>s<sup>-1</sup>,  $1.86 \times 10^{-41}$  cm<sup>3</sup> molecular<sup>-1</sup>s<sup>-1</sup>, and  $2.82 \times 10^{-40}$  cm<sup>3</sup> molecular<sup>-1</sup>s<sup>-1</sup>, respectively. The hydrolysis products of ethylene terephthalate dimer are mainly terephthalic acid and ethylene glycol; the alcoholysis products mainly include terephthalate dimer are dimethyl terephthalate and ethylene glycol; and ammonolysis products mainly include terephthalate dimer are dimethyl terephthalate divelae the glycol; show that the Gibbs free energy change of hydrolysis/alcoholysis/ammonolysis is negatively correlated with temperature and an increase in temperature enhance the spontaneity of the reaction.

# 1. Introduction

Polyethylene terephthalate (PET) is one of the most common and significant thermoplastics. Due to its excellent physical and chemical properties, such as being lightweight, having good heat resistance and dimensional stability, and being resistant to chemicals, among others, it is widely used in various industries (Das et al., 2021; Jankaukaite et al., 2016; Samak et al., 2020). With the mass production and application of PET plastic, the amount of PET plastic waste has increased sharply, which has not only seriously polluted the environment but also caused a waste of resources (Al-Sabagh et al., 2016; Raheem et al., 2019; Sojobi et al., 2016). Due to its enduring stability, a substantial portion of utilized PET requires several centuries to naturally degrade (Wei et al., 2017). Furthermore, the degradation process can lead to the fracturing of PET into particles and even microplastics. These microplastics accumulate in soil and even flow into rivers, posing threats to the health and

safety of both aquatic and terrestrial life (Patidar et al., 2023a, 2023b; Perumpully et al., 2023). In the context of carbon neutrality, the degradation and recycling of PET plastic waste have become important issues around the world (Lee et al., 2022). On the one hand, the chemical conversion of PET waste plastic has a high atom economy, which can greatly reduce the impact of plastic waste on the environment. On the other hand, it also extends the service life of PET plastics. Therefore, effective recycling of valuable chemical raw materials from PET waste plastic is of great significance in contributing to a circular economy and reducing the environmental impact of plastic waste. Many conversion processes have been developed to recycle waste PET. Pyrolysis is a method of converting high-molecular-weight polymers into recyclable minor molecular compounds under anaerobic conditions. For instance, PET can decompose into 4-(methoxycarbonyl) benzoic acid and benzoic acid by pyrolysis, while caprolactam is the main pyrolysis product of nylon 6. These monomers can then be purified and reused in the

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production of new PET or nylon polymers. (Kumartasli et al., 2020; Wang et al., 2023). In recent years, pyrolysis has been considered one of the most effective methods to deal with PET waste plastic, which has important practical significance for reducing energy pressure and environmental pollution (Ayodeji and Oni, 2019; Dhahak et al., 2020; Xue et al., 2017). However, the process of polymer pyrolysis into small molecule compounds requires higher temperatures, and the complex product components result in a high cost and difficulty of recycling waste plastic raw materials. An appropriate change in the degradation conditions can effectively control the composition and distribution of the products and reduce energy consumption in the process of degradation (Barth et al., 2015; Songip et al., 1994). Water (H<sub>2</sub>O) is the most important and non-toxic solvent in nature, which comes from a wide range of sources and does not even need to be removed from the products (Sako et al., 1997). Methanol (CH<sub>3</sub>OH) is an important organic chemical material and plays an important role in the decomposition reaction medium (Genta et al., 2007). Ammonia (NH<sub>3</sub>) is a reducing gas, and the presence of ammonia can promote the breaking of acyl-oxygen bonds in the ester bonds of polymer backbones to form chemical intermediates with terminal hydroxyl groups (Yang, 2012). Therefore, hydrolysis/alcoholysis/ammonolysis have been considered as one of the most effective feasible proposals to deal with PET waste plastic.

At present, there have been many macroscopic experimental studies on PET hydrolysis/alcoholysis/ammonolysis (Abedsoltan et al., 2023; Du et al., 2020). Ügdüler et al. (2020) have demonstrated the efficient recycling of multilayer and colored PET plastic waste through a two-step aqueous alkaline hydrolysis process. They successfully converted PET waste into monomers such as ethylene glycol and terephthalic acid, achieving yields of up to 95 % under mild conditions (≤80 °C, atmospheric pressure). Colnik et al. (2021) performed hydrolysis experiments on PET waste using sub- and supercritical water in a batch reactor. The results show that a hydrolysis temperature of 300 °C can obtain a high yield and purity of terephthalic acid. Ambrose-Dempster et al. (2023) have significantly improved the degradation efficiency of PET through a mechanoenzymatic hydrolysis approach. Pereira et al. (2023) used post-consumer PET hydrolyzed in pure water and at neutral PH over a wide range of temperatures (190-400 °C) and pressures (1-35 MPa) to produce terephthalic acid in a short reaction time. Yao et al. (2021) discovered the reaction mechanism of the PET alcoholysis collaborative catalytic system and obtained the action mechanism of PET at different interfaces of zinc oxide (ZnO) and the first-order reaction kinetics of PET alcoholysis. The experimental results showed that ZnO/SBA-15 has high catalytic activity. Yang et al. (2012) investigated the ammonolysis of PET catalyzed by metal function ionic liquid and showed that the ammonolysis of PET could generate the corresponding terephthalamide and ethylene glycol. Xie et al. (2024) effectively converted PET into terephthalonitrile with a high yield of 32.5 % at 550 °C using urea-assisted in-situ catalytic pyrolysis. They also elucidated the pivotal role of active ammonia in PET depolymerization and found that the ammonolysis of PET was more likely to form amide rather than aromatic ammonium salt. A recent study by Liang et al. (2024) has made significant strides in this area by developing a catalyst-free ammonolysis process for the conversion of PET waste into terephthalamide with a one-step reaction process at 40-120 °C. This approach can simplify the recycling process by eliminating the need for catalysts and solvents, yielding more than 95 mol% and more than 95 % purity of terephthalamide.

Compared with the experimental research, the theoretical study by quantum chemistry methods can interpret the PET hydrolysis/alcoholysis/ammonolysis reaction processes and the formation and evolution mechanisms of the product in more detail. A better understanding of the mechanisms underlying PET hydrolysis/alcoholysis/ammonolysis at the molecular level is very important for optimizing these methods. Hence, it is necessary to further study its mechanism in order to efficiently converting PET into high-value chemical raw materials. condensation of terephthalic acid and ethylene glycol (Zimmermann et al., 2020). The microscopic mechanisms of polymers degradation are usually studied by various model compounds (Huang et al., 2022), and ethylene terephthalate dimer contains all the chemical characters appearing in PET, thus, ethylene terephthalate dimer was selected as a PET model compound in order to study the hydrolysis/alcoholysis/ ammonolysis mechanisms of PET in this work. We carried out thermodynamic calculations using density functional theoretical methods, and analysis of the possible reaction paths in hydrolysis/alcoholysis/ ammonolysis of ethylene terephthalate dimer. Finally, we calculated the effect of temperature on the main pathways of hydrolysis/alcoholysis/ ammonolysis. These studies of the thehydrolysis/alcoholysis/ammonolysis mechanisms of ethylene terephthalate dimer using quantum chemical method are intended to be an important guide for energy conversion and recycling technology for PET waste.

# 2. Computational methods

#### 2.1. Electronic structure calculations

All density functional theory (DFT) calculations were performed using Gaussian 16 program (Frisch et al., 2016). Previous studies have shown that the M06 meta function performs exceptionally well in databases involving main-group thermochemistry, kinetics, and noncovalent interactions (Zhao et al., 2008). Therefore the geometries of reactions, intermediates, transition states, and products were optimized using the density functional M06 method using the cc-pVDZ base set. The above methods have been successfully applied to the mechanistic study of pyrolysis of organic compounds (Maftei et al., 2018; Wang et al., 2023a, 2023b). Although this study employed conventional hybrid DFT method (M06) for geometry optimization and calculation of thermodynamic and kinetic parameters, it is important to note that the latest research shows newer range-separated DFT methods (such as CAM-B3LYP and wB97X) give more accurate calculations of HOMO-LUMO gaps compared to conventional hybrid functionals (Senan et al., 2023). The frequency was calculated at the same calculation level to obtain the thermodynamic parameter values at the standard conditions (298.15 K, 1 atm), and the zero vibration energy (ZPE) correction is considered for the thermodynamic quantity. The vibration frequencies of the reactants, intermediates, and products are all positive, and all transition states have one and only one imaginary frequency, which is verified by a GaussView program or calculation of intrinsic reaction coordinates (IRC) to ensure the correct transition states for the products and reactants. The enthalpy energy difference between the transition state ( $E_{TS}$ ) and the reactant ( $E_R$ ) under 298 K and 1 atm is taken as the potential barrier of the reaction ( $\Delta E$ ), and the enthalpy energy difference between the product  $(E_{\rm P})$  and the reactant  $(E_{\rm R})$  is taken as the enthalpy change of the reaction. We assumed that all the decomposition pathways are in the ground state (single state).

#### 2.2. Kinetic computations

Canonical transition state theory (TST) (Bao and Truhlar, 2017) and the Eckart correction was used to calculate the rate constant from equation (1) by the kinetic program KiSThelP (Canneaux et al., 2014):

$$k^{\text{TST}} = \kappa \sigma \frac{k_B T}{h} \left(\frac{RT}{P^0}\right)^{\Delta n} e^{-\Delta G^{0, \neq}/k_B T}$$
(1)

where h,  $k_B$ , and T denote the Planck's constant, Boltzmann's constant, and the temperature, respectively;  $RT/P^0$  means the inverse of Molar concentration;  $\Delta n$  equals 0 or 1 for unimolecular and bimolecular reactions, respectively; and  $\Delta G^{0,\neq}$  is the Gibbs free energy of activation;  $\sigma$ is the degeneracy of the reaction pathway as:

$$\sigma = \frac{\sigma_{\rm rot,R}}{\sigma_{\rm rot,TS}} \tag{2}$$

In equation (2),  $\sigma_{rot,R}$  and  $\sigma_{rot,TS}$  are the rotational symmetry numbers of reactants and transition states. Additionally, zero point energies were scaled by a factor of 0.984 to reduce systematical error and account for anharmonic effect (Alecu, 2010).

#### 3. Results and discussion

#### 3.1. Hydrolysis mechanisms of PET dimer

PET hydrolysis studies have shown that PET hydrolysis is mainly carried out through the synergistic reaction mechanism of  $C_{acyl}$ -O bond breaking in the main chain (Wang et al., 2011; Han et al., 2018; Ügdüler et al., 2020; Pereira et al., 2023). In addition, H<sub>2</sub>O can dissociate weakly into H<sup>+</sup> and OH<sup>-</sup>. Based on the study by Xu et al. (2020), the influence of H<sup>+</sup> produced by the ionization of H<sub>2</sub>O is fairly limited, so we ignored the ionization of water during the calculation. Therefore, this paper mainly considers the concerted reaction mechanisms through 4-membered cyclic transition states for the C<sub>acyl</sub>-O bond breaking in the main chain of PET dimer, and we design three possible reaction pathways, as shown in Scheme 1 (Path (1)). The optimized structures of the transition states are shown in Fig. 1, and the reaction energy barriers are shown in Fig. 2.

In the reaction pathway (1-a), PET dimer 1 reacts with  $H_2O$  through a 4-membered cyclic transition state ( $TS_1$ ) to form terephthalic acid 2 and bis (2-hydroxyethyl) benzene-1,4-dicarboxylate 3. As shown in Fig. 1, the length of the O–H bond in  $H_2O$  molecules was 0.960 Å, and

Path(1)

the length of the Cacyl-O bond (C(4)-O(5)) in PET dimer was 1.347 Å; nevertheless, the length of the O-H bond in transition state TS1 increased to 1.183 Å, and the length of the Cacyl-O bond (C(4)-O(5)) is increased to 1.759 Å. In this hydrolysis reaction mechanism, -OH in H<sub>2</sub>O would attack the C(4) atom in the Cacyl-O bond, causing the cleavage of the C(4)-O(5) bond. At that time, -OH binds to the carbon atom C(4) of the carbonyl group to form terephthalic acid, while the remaining H atom binds to O(5) to form a hydroxyl terminal compound. This process requires overcoming a barrier height of 165.6 kJ/mol and emitting a lower heat of 5.2 kJ/mol. Bis (2-hydroxyethyl) benzene-1,4dicarboxylate 3 can hydrolyzes to ethylene glycol 4 and ethylene terephthalate 5 via TS<sub>2</sub>, with an energy barrier of 156.6 kJ/mol. Next, the ethylene terephthalate 5 is further degraded into the main PET products, i.e., terephthalic acid  ${\bf 2}$  and ethylene glycol,  ${\bf 4}$  in the presence of  $H_2O$  via TS<sub>3</sub>. In the reaction pathway (1-b), PET dimer 1 can also be hydrolyzed into ethylene terephthalate 5 via the 4-membered cyclic transition state (TS<sub>4</sub>), with an energy barrier of 165.5 kJ/mol. In reaction pathway (1-c), PET dimer 1 decomposes into ethylene glycol 4 and 1,2-bis-(4-carboxybenzoyloxy)-ethane 6 in the presence of H<sub>2</sub>O via TS<sub>5</sub>, with an energy barrier of 166.0 kJ/mol. Compound 6 can be further hydrolyzed via TS<sub>6</sub> leading to the formation of terephthalic acid 2 and ethylene terephthalate 5, with a slightly lower energy barrier (155.3 kJ/mol).

In the hydrolysis of PET dimer, the energy barriers for hydrolysis at the positions in the middle and terminal of the main chain are essentially the same, which are 165.6, 165.5, and 166.0 kJ/mol, respectively. This result showed that the hydrolysis reaction of PET may be caused by the random cracking of the  $C_{acyl}$ -O bond in the main chain, resulting in the formation of main products such as terephthalic acid **2** and ethylene



Scheme 1. Possible reaction paths for PET dimer hydrolysis.













TS6



Fig. 1. Geometrically optimized structures of all transition state. The crucial distance (Å) are marked.





TS12





**TS14** 





TS16



TS17







Fig. 1. (continued).



glycol **4**, which is consistent with the results of related PET hydrolysis experiments (Wang et al., 2011; Han et al., 2018; Ügdüler et al., 2020; Pereira et al., 2023).

# 3.2. Alcoholysis mechanisms of PET dimer

Based on related alcoholysis experiments (Lorenzetti et al., 2006; Dimitrov et al., 2013; Shojaei et al., 2020), the alcoholysis reaction of PET dimer may involve three distinct routes, as illustrated in Scheme 2. The optimized structures of transition states are shown in Fig. 1 and reaction energy barriers are shown in Fig. 3. In the reaction path (2-a), PET 1 and CH<sub>3</sub>OH pass through the 4-centered transition state (**TS**<sub>7</sub>) to form mono-methyl terephthalate 7 and bis (2-hydroxyethyl) benzene-1,4-dicarboxylate 3, which need to overcome a barrier height of 161.3 kJ/mol with an exothermic of -6.6 kJ/mol. As shown in Fig. 1, the O–H bond length of CH<sub>3</sub>OH molecule was optimized to 0.964 Å, and the length of the C<sub>acyl</sub>-O bond (C(4)-O(5)) in PET dimer was 1.347 Å; whereas the length of the O–H bond becomes 1.189 Å, and the length of the acyl oxygen bond (C(4)-O(5)) becomes 1.771 Å in the transition state **TS<sub>7</sub>**. In this alcoholysis reaction mechanism,  $-OCH_3$  in CH<sub>3</sub>OH would attack the C(4) atom in the carbonly group, causing the breakage of the C(4)-O(5) bond. At the same time, the remaining H atom in CH<sub>3</sub>OH could combine with the O(5) atom, and then Bis (2-hydroxyethyl) benzene-1,4-dicarboxylate **3** and mono-methyl terephthalate **7** were



Fig. 2. Reaction energy barriers for the hydrolysis of PET dimer.



Scheme 2. Possible reaction paths for ethylene terephthalate dimer alcoholysis.

Path(3)



Scheme 3. Possible reaction paths for ammonolysis of PET dimer.

obtained. Bis (2-hydroxyethyl) benzene-1,4-dicarboxylate 3 is further alcoholized to generate ethylene glycol 4 and diethylene glycol terephthalate 8 via TS8, with a barrier height of 147.2 kJ/mol. Next, diethylene glycol terephthalate 8 can decompose into ethylene glycol and dimethyl terephthalate 9 with the participation of CH<sub>3</sub>OH via TS<sub>9</sub>, which are the main products of PET alcoholysis. The required activation energy is 147.0 kJ/mol. In the reaction path (2-b), PET dimer is able to form diethylene glycol terephthalate 8 and ethylene terephthalate 5 with the participation of CH<sub>3</sub>OH via TS<sub>10</sub>, and ethylene terephthalate 5 is further alcoholized and decomposed into mono-methyl terephthalate 7 and ethylene glycol 4 via  $TS_{11}$ . The energy barriers of the above processes are 161.0 kJ/mol and 146.7 kJ/mol, respectively. In the reaction path (2-c), PET dimer 1 and CH<sub>3</sub>OH can be degraded into ethylene glycol 4 and compound 10 via  $TS_{12}$ , with a reaction energy barrier of 145.5 kJ/mol. Compound 10 is further alcoholized by TS13 to form mono-methyl terephthalate 7 and diethylene glycol terephthalate 8 with an energy barrier of 145.8 kJ/mol. In addition to this, compound 10 can also be alcoholized to generate dimethyl terephthalate and ethylene glycol by  $TS_{14}$ , with an energy barrier of 145.8 kJ/mol, which is identical to that of  $TS_{13}$ .

In the alcoholysis of PET dimer, the reaction energy barriers for the breakage of the middle or terminal  $C_{acyl}$ -O bonds in the main chain is 145.5–161.3 kJ/mol. This indicates that the alcoholysis process of PET dimer may be multiple alcoholysis of the ester bond at any position of the main chain, leading to the formation of the main products (such as dimethyl terephthalate **9** and ethylene glycol **4**), which is basically in accordance with the results of the related PET alcoholysis experiments (Lorenzetti et al., 2006; Dimitrov et al., 2013; Shojaei et al., 2020).

# 3.3. Ammonolysis mechanism of ethylene terephthalate dimer

According to the experimental results of PET ammonolysis under an ammonia atmosphere (Spychaj et al., 2001; Shukla and Harad, 2006; Xie et al., 2024), three possible reaction paths for the ammonolysis of PET



Fig. 3. The energy barrier for PET dimer alcoholysis reaction



Fig. 4. Ammonolysis reaction energy barriers of PET dimer.

dimer were designed as shown in Scheme 3. Fig. 1 shows the optimal structure of the transition states; Fig. 4 and Fig. 5 describe a schematic diagram for the reaction energy barriers of PET dimer ammonolysis. In the reaction pathway (3-a), PET dimer 1 ammonolysis to terephthalic acid monoamide 11 and bis (2-hydroxyethyl) benzene-1,4-dicarboxylate 3 via TS<sub>15</sub>. Before the reaction, the N–H bond length of the NH<sub>3</sub> molecule was optimized to be 1.022 Å, and the length of the C<sub>acyl</sub>-O bond (C(4)-O(5)) in the PET dimer was 1.347 Å. In the transition state, the N–H bond length of TS<sub>15</sub> becomes 1.146 Å, and the acyl oxygen bond (C(4)-O(5)) bond length becomes 1.894 Å. In this reaction mechanism, –NH<sub>2</sub> in NH<sub>3</sub> would attack the C(4) atom in the C<sub>acyl</sub>-O bond to form a terephthalic acid monoamide, while the remaining H atom combines with O(5) to form a bis (2-hydroxyethyl) benzene-1,4-dicarboxylate, and the C(4)-O(5) bond would be broken. This process required overcoming a barrier of 148.3 kJ/mol, which is in correct

agreement with the value obtained by Xie et al. (2024) at the B3P86/ 6–31++G(d,p) level of theory (151.5 kJ/mol). Terephthalic acid monoamide **11** undergoes H transfers (**TS**<sub>16</sub>) in the amino group to form compound **12** by overcoming an energy barrier of 165.7 kJ/mol and endothermic by 59.5 kJ/mol. And then, –OH and the H (on the N atom) of compound **12** dehydration through  $\beta$ -elimination (**TS**<sub>17</sub>) yield H<sub>2</sub>O and 4-cyanobenzoic acid **13**, with reaction energy barriers of 305.6 kJ/ mol and endothermicity of 70.4 kJ/mol. Note that the barrier heights given by Xie et al. (2024) are 174.5 and 310.9 kJ/mol, in agreement with our values. Further, a ammonolysis reaction may occur in terephthalic acid monoamide **11** to form terephthalamide **15** and H<sub>2</sub>O by **TS**<sub>18</sub> (170.4 kJ/mol). In comparison, reactions for dehydration ( $\beta$ -elimination) and H transfers have high energy barriers as well as being heat absorbing, which are not advantageous. This signifies that PET dimer readily generates terephthalamide **15** through the ammonolysis



# Fig. 5. H transfer and dehydration energy barrier in Scheme 3.

reaction. Xie et al. (2024) reached the same conclusion through theoretical calculation. This result is also consistent with the experimental observation of Liang et al. (2024). Bis (2-hydroxyethyl) benzene-1,4dicarboxylate 3 is degraded to ethylene glycol 4 and compound 14 with the participation of  $NH_3$  through  $TS_{19}$ , with a reaction energy barrier of 154.6 kJ/mol. Compound 14 was further ammolyzed to form ethylene glycol and terephthalamide 15 by TS<sub>20</sub>, with an energy barrier of 154.7 kJ/mol. Terephthalamide 15 isomerizes to compound 16 through H transfers (TS<sub>21</sub>) in amino group by overcoming an energy barrier of 165.2 kJ/mol and endothermic by 60.6 kJ/mol. Subsequently, compound 16 dehydration (TS22) to form 4-Cyanobenzamide 17 and H<sub>2</sub>O, the energy barriers is 306.2 kJ/mol. It can be seen from the optimized structures of  $TS_{21}$  and  $TS_{22}$  that the H atom from the amide group transfers from the N atom to the O atom to form an OH group, and then dehydration can occur between the OH group and the H atom on the N atom to form 4-cyanobenzamide 17. For TS20, Xie et al. (2024) computed energy barriers equal to 164.0 kJ/mol, in good agreement with our values. However, for TS21 and TS22, large differences are observed (17.6 and 13.9 kJ/mol). In the same way, 4-cyanobenzamide 17 can undergo H transfer (TS23) and dehydration reaction (TS24), leading to the formation of H<sub>2</sub>O and 1,4-diisocyanobenzene 19 with energy barriers of 166.9 kJ/mol and 307.3 kJ/mol, respectively. As expected, dehydration remains the most difficult process, requiring an energy barrier of more than 300 kJ/mol. This indicated that terephthalamide 15 is hard to convert to 1,4-diisocyanobenzene 19, which is consistent with the previous study (Xie et al., 2024). In the reaction pathway (3-b), PET dimer 1 is decomposed into compound 14 and ethylene terephthalate 5 with the participation of NH<sub>3</sub> via TS<sub>25</sub>, which required overcoming a barrier of 148.2 kJ/mol. Ethylene terephthalate 5 was further ammoniated into ethylene glycol 4 and terephthalic acid monoamide 11 via TS<sub>26</sub>, with an energy barrier of 154.3 kJ/mol. In the reaction pathway (3-c), compounds 1 and NH<sub>3</sub> were degraded to ethylene glycol 4 and compound 20 via  $TS_{27}$ , with an energy barrier of 155.0 kJ/mol. Compound 20 can be ammoniated by TS28 to form terephthalic acid monoamide 11 and compound 14. An additional possible pathway for compound 20 is  $TS_{29},$  leading to terephthalamide 15 and ethylene terephthalate 5. The reaction energy barriers for TS<sub>28</sub> and TS<sub>29</sub> are 145.8 kJ/mol and 150.0 kJ/mol, respectively. These intermediates (5, 11, and 14) can easily react by ammonolysis to form terephthalamide 15 further.

In the ammonolysis of PET dimer, the reaction energy barriers of ammonolysis reactions at the  $C_{\rm acyl}\mbox{-}O$  bond in the middle or terminal

position of the main chain were 148.3–155.0 kJ/mol. This indicates that the ammonolysis of PET may be caused by multiple degradations of the  $C_{acyl}$ -O bond at any position of the main chain, resulting in the formation of main products such as terephthalamide **15** and ethylene glycol **4**, which is basically the same as the results of relevant PET ammonolysis experiments (Spychaj et al., 2001; Shukla and Harad, 2006; Xie et al., 2024).

By comparing the computational results of the hydrolysis/alcoholysis/ammonolysis of the PET dimer to the pyrolysis, it can be seen that the reaction energy barriers of the hydrolysis/alcoholysis/ammonolysis of the PET dimer are lower than the thermal decomposition (the energy barriers of concerted reaction through the six-membered ring and fourmembered ring transition states and free radical reaction are 184.0, 267.0, and 345.0 kJ/mol, respectively.) (Huang et al., 2022). As can be observed, hydrolysis/alcoholysis/ammonolysis can reduce the energy barriers of the main reaction steps of the degradation of PET dimer to a certain extent, making the reaction easier to proceed. Besides, calculation data show that the reaction energy barriers for the cleavage of PTE dimer in NH<sub>3</sub> atmosphere are the smallest, followed by cracking in CH<sub>3</sub>OH medium and H<sub>2</sub>O medium.

#### 3.4. Effect of different temperature on hydrolysis/alcoholysis/ ammonolysis mechanisms of PET dimer

# 3.4.1. Effect of different temperature on hydrolysis/alcoholysis/ ammonolysis thermodynamics of PET dimer

This work considers the influence of temperature on the thermodynamics of ethylene terephthalate dimer hydrolysis/alcoholysis/ammonolysis mechanism. To study a reaction from the perspective of thermodynamics, it is only necessary to consider the beginning and end states of the reaction without considering its intermediate process. We calculated the reaction free energy ( $\Delta G$ ) and enthalpy change ( $\Delta H$ ) parameters of the PET dimer degradation process under different temperature conditions (298, 400, 500, 600, 700, 800, and 900 K) to estimate the feasibility of the reaction. The free energy change of the reaction  $\Delta G$  is an important thermodynamic parameter used to determine the direction of spontaneous reactions and the reactant conversion to products when the reaction reaches equilibrium. When free energy change  $\Delta G$  is less than zero, the reaction can be spontaneous, and the smaller the reaction  $\Delta G$ , the greater the conversion of reactant when the reaction reaches equilibrium. From the perspective of reaction energy,  $\Delta H$  greater than 0 indicates an endothermic reaction, whereas an

Table 1

$\Delta H(kJ \cdot mol^{-1})/\Delta G(kJ \cdot mol^{-1})/\Delta S(J \cdot mol^{-1} \cdot K^{-1})$ of	PET dimer during hydrolysis/alcoholysis/	'ammonolysis processes at different temperatures.
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T(K)	Hydrolysis/a	Hydrolysis/alcoholysis/ammonolysis(Path (1)/ Path (2)/ Path (3))							
	$\Delta H/$	$\Delta G/$	$\Delta S/$	$\Delta H/$	$\Delta G/$	$\Delta S/$	$\Delta H/$	$\Delta G/$	$\Delta S/$
298	0.0	-15.8	53.1	-16.4	-20.5	13.8	49.4	31.0	61.7
400	-10.5	-28.7	45.5	-16.4	-21.9	13.8	48.6	24.9	59.3
500	-12.6	-33.1	41.0	-16.4	-23.3	13.8	48.4	19.0	58.8
600	-14.1	-37.0	38.0	-16.4	-24.7	13.8	48.4	13.1	58.8
700	-15.3	-40.7	36.3	-16.3	-26.0	13.9	48.6	7.2	59.1
800	-16.1	-44.3	35.3	-16.2	-27.4	14.0	48.9	1.3	59.5
900	-16.8	-47.8	34.4	-16.2	-28.8	14.0	49.1	-4.6	59.7

exothermic reaction (Huang et al., 2015). Table.1 shows the enthalpy change ( $\Delta H$ ), free energy change ( $\Delta G$ ) and entropy change ( $\Delta S$ ) of the degradation process of PET dimer during hydrolysis/alcoholysis/ ammonolysis at different temperatures.

As can be seen clearly from the data in Table 1, in the hydrolysis of PET dimer  $\Delta G$  and  $\Delta H$  are negative above 298 K, and both  $\Delta G$  and  $\Delta H$ decrease with increasing temperature. Therefore, it is speculated that the PET hydrolysis reaction is more spontaneous above 298 K and increasing the temperature can increase the spontaneity of PET hydrolysis. In the PET dimer alcoholysis reaction, the temperature dependence of  $\Delta H$  is limited, which means that the change in  $\Delta H$  with increasing temperature is small.  $\Delta H$  and  $\Delta G$  are always less than zero, and  $\Delta G$ decrease with increasing temperature, similar to hydrolysis. As a result, it is speculated that PET hydrolysis/alcoholysis could be a type of spontaneous exothermic reaction. In the process of PET dimer ammonolysis, the values of  $\Delta H$  are positive at all reaction temperatures, indicating an endothermic nature of these chemical reactions so it is necessary to intake thermal energy from outside to push the processes of PET ammonolysis. The value of  $\Delta G$  goes negative at about 900 K. Therefore, it is speculated that PET ammonolysis can be spontaneous at 900 K or higher. In addition, temperature also has little effect on  $\Delta H$  in the ammonolysis process of PET dimer.  $\Delta S$  is always positive in hydrolysis/alcoholysis/ammonolysis, but the entropy effect is more favorable to PET ammonolysis. The revelation of this result may help chemical scientists optimize the chemical recovery process of PET by developing a more rational reaction temperature, and applying it in practical industrial. For example, increasing the reaction temperature to about 900 K during PET ammonolysis can tilting the chemical balance toward the product. This will benefit to reduced the required of catalytic, increased the yield, thus the production cost can be reduced and the efficiency improved. However, it is also necessary to pay attention to the increase in equipment costs and possible side effects caused by rising

#### Table 2

Rate constant (*k*) and products branching ratio (R) for the initial reaction at 298 K (the unit of rate constants is  $\text{cm}^3$  molecular<sup>-1</sup>s<sup>-1</sup>).

Paths	k <sub>298K</sub>	R	k <sub>tot</sub>
PET dimer + H <sub>2</sub> O $\rightarrow$ IM3 + IM2	4.85E-	0.321	$k_{tot\_hydrolysis} = 1.51\text{E-43}$
	44		
PET dimer + $H_2O \rightarrow 2IM5$	9.09E-	0.602	
	44		
PET dimer + $H_2O \rightarrow IM4 + IM6$	1.15E-	0.077	
	44		
PET dimer + CH <sub>3</sub> OH $\rightarrow$ IM3 +	1.73E-	0.009	$k_{tot alcoholysis} = 1.86E-41$
IM7	43		
PET dimer + CH <sub>3</sub> OH $\rightarrow$ IM8 +	4.63E-	0.002	
IM5	44		
PET dimer + CH <sub>3</sub> OH $\rightarrow$ IM4 +	1.84E-	0.988	
IM10	41		
PET dimer + $NH_3 \rightarrow IM3 + IM11$	1.14E-	0.403	$k_{tot ammonolysis} = 2.82E$ -
	40		40
PET dimer + $NH_3 \rightarrow IM14 + IM5$	1.50E-	0.534	
<b>3</b>	40		
PET dimer + $NH_3 \rightarrow IM4 + IM20$	1.77E-	0.063	
	41		

#### temperatures.

# 3.4.2. Effect of different temperature on hydrolysis/alcoholysis/ ammonolysis kinetics of PET dimer

The conventional TST was used to obtain the rate constants of the reactions of PET hydrolysis/alcoholysis/ammonolysis in the KiSThelP program. The rate constants were computed using frequencies, energy barriers, and the geometries of the transition states, and the Eckart correction was applied. The rate constants at 298 K for the initial reactions of PET hydrolysis/alcoholysis/ammonolysis are given in Table 2. Additionally, the branching ratios (R) of the initial reactions of hydrolysis/alcoholysis at 298 K are also listed in Table 2. The branching ratios are calculated by dividing the reaction rate constants for each initial reaction by the total reaction rate constant ( $R = k/k_{tot}$ ), and the hydrolysis, alcoholysis, and ammonolysis are calculated separately.

To assess the relative importance of the different conditions for the degradation of PET dimer at different temperatures, the total rate constants for the hydrolysis/alcoholysis/ammonolysis pathways ( $k_{tot_hydrolysis}$ ,  $k_{tot_alcoholysis}$ , and  $k_{tot_ammonolysis}$ ) were calculated over a range of temperatures, from 298 to 498 K in 20 K increments, as shown in Fig. 6. The results show that the total rate constants of hydrolysis/alcoholysis/alcoholysis/ammonolysis increases with increasing temperature in the rage of 298–498 K. Total rate constants of the ammonolysis reactions of PET are generally one to two orders of magnitude higher than hydrolysis and alcoholysis at all temperatures. This indicates that ammonolysis is more likely to occur kinetically than hydrolysis and alcoholysis. The kinetic findings are also consistent with the above reaction mechanisms.

This study employs DFT methods to calculate thermo-kinetic parameters to explain the degradation mechanism of PET plastic waste. However, the DFT methods are an approximate approach for solving the electronic structure of multi-electron system. This could potentially result in reduced precision of the computed outcomes and the



Fig. 6. Calculated rate constants for the initial reaction of PET hydrolysis/ alcoholysis/ammonolysis between 298 and 498 K and 1 atm.

introduction of errors, thereby affecting the comprehensive comprehension and forecasting of chemical reactions. Additionally, it is not pragmatic to calculate the thermo-kinetic parameters for PET polymers due to the high cost of DFT computation. The PET model compound (PET dimer) was used to loosely explain the degradation mechanism of PET polymers. Despite the fact that achieving quantitative correctness in macromolecular systems is still a challenge, the qualitative insights provided by our theoretical calculations are reliable. Moreover, our study offers a valuable theoretical framework that can guide future experimental and computational research in the field of PET recycling.

#### 4. Conclusions

In this study, the elementary steps associated with hydrolysis/alcoholysis/ammonolysis pathways for the common and significant thermoplastics PET, were successfully probed via DFT method M06/ccpVDZ, analyzed their thermodynamic and kinetic feasibility. Mechanism study shows that the main products of hydrolysis of ethylene terephthalate dimer are terephthalic acid and ethylene glycol; the main products of alcoholysis are dimethyl terephthalate and ethylene glycol; and the main products of ammonolysis are terephthalamide and ethylene glycol. The analysis about thermodynamics and kenitics reveals that the energy barrier for the degradation process of PET dimer can be reduced under hydrolysis/alcoholysis/ammonolysis conditions compared to pure pyrolysis, facilitating the reaction. And a rise in reaction temperatures can boost the spontaneity of the reaction and the reaction rate constants during the hydrolysis/alcohololysis/ammonolysis of PET. This study can serve as a theoretical model and guide for experimental and industrial applications in the filed of PET recycling.

Despite the theoretical potential of hydrolysis/alcohololysis/ ammonolysis, hydrolysis/alcohololysis/ammonolysis usually requires catalysts and high reaction pressures to increase the reaction rate, so there are still some challenges in practical applications. Future research needs to concentrate on screening catalysts, optimizing reaction conditions, improving product recovery rates, and reducing overall processing costs.

#### CRediT authorship contribution statement

Jinbao Huang: Data curation, Writing – original draft. Weifeng Xu: Visualization, Investigation. Yang Long: Visualization, Investigation. Yan Zhu: Writing – review & editing. Song Chen: Writing – review & editing. Wenjing Duan: Conceptualization, Methodology. Jiankai Ou: Conceptualization, Methodology. Hong Wang: Formal analysis. Changwen Dong: Formal analysis. Shuang Tian: Supervision.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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