Thermal decomposition mechanisms of poly(vinyl chloride): A computational study

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ABSTRACT

The studies on the pyrolysis mechanisms of waste PVC contribute to development and application of pyrolysis technology for mixed waste plastics. In the article, the thermal decomposition mechanisms of model compound of poly(vinyl chloride) (PVC) have been investigated by employing density functional theory methods at M06-2X/6–31++G(d,p) level in order to illuminate the elimination of HCl and the formation of hydrocarbons. Various possible pyrolysis paths for the formation of main products were proposed, and the thermodynamic and kinetic parameters in every path were calculated. The calculation results show that the HCl elimination can occur through the concerted reaction and the energy barrier of HCl elimination changes from 167.4 to 243.3 kJ/mol; allyl group can obviously reduce the activation energy of HCl elimination, and the branched-chain can lower the energy barrier of HCl elimination at the carbon sites near the branch chain; a free radical is more easily converted into aromatic compound through a series of isomerizations, cyclization and dehydrogenation; the conjugated polyene could be decomposed in parallel reaction channels: one is the evolution of aromatics, another is the formation of small molecule products. The above analysis is consistent with previous experimental results and analysis.

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1. Introduction

Plastic products are highly convenient for people's use on account of their resistance to degradation, versatility, light weight and low price. The production of plastic increased on an average of 10% every year on a global basis since 1950 as continuous innovation and research for better product in the field occurred (Diaz Silvarrey and Phan, 2016). The short cycle life of plastics leads to the emergence of a large number of plastic wastes. The municipal plastic wastes (MPW) comprise a mixture of thermoplastics (such as polyethylene, PE; polypropylene, PP; polystyrene, PS; poly(vinyl chloride), PVC; and polyethylene terephthalate, PET). The rate of MPW generation has increased steadily at 5% per year while that of MPW recycling is only at 3% per year (Singh and Ruj, 2016). The remains are either incinerated or disposed in landfills. Pyrolysis, a thermochemical decomposition, provides an excellent alternative to transform MPW into energy fuels or valuable chemicals.

There have been a number of researches on the pyrolysis of individual and mixed plastics with and without PVC (Aboulkas et al., 2010; Kim and Kim, 2004; Kumagai et al., 2015; Zheng et al., 2007). It is well known that the thermal decomposition of mixed plastics containing PVC generates HCl, which is corrosive, and some chlorinated hydrocarbons, which act as precursors of toxic emissions such as polychlorinated dibenzodioxins (PCDD), dibenzofurans (PCDF) and polychloro biphenyls (PCB) upon combustion afterwards (Bhaskar et al., 2005; Cao et al., 2016; Shen et al., 2016). Among all sorts of plastics, PVC is one of the most important but also potential environmentally harmful polymers for the content of chlorine. Therefore, studies on the thermal decomposition mechanism of PVC are an important consideration in developing pyrolysis technology for mixed waste plastics. Yuan et al. (2014) reported high efficiency chlorine removal from polyvinyl chloride (PVC) pyrolysis with a gas-liquid fluidized bed reactor, and the experimental results showed that dechlorination efficiency is mainly temperature dependent and 300 °C is a proper reaction temperature; under this temperature 99.5% of Cl removal efficiency can be obtained within reaction time around 1 min after melting is completed. Zhou et al. (2016) investigated the influence

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of process conditions on the formation of polycyclic aromatic hydrocarbons (PAH) during the pyrolysis of PVC; slow pyrolysis produced higher HCl yield, and lower gas and tar yield than fast pyrolysis; the PAH yield obtained from the slow pyrolysis was much lower compared to fast pyrolysis. The reaction kinetics of the thermal decomposition of PVC was studied by Castro et al. (2012), and a kinetic model was developed for the decomposition temperatures lower than 340 °C, in which almost all chlorine is removed from the pure PVC, with an activation energy of 133.8 kJ/mol. Gui et al. (2013) investigated the effects of peak temperature, holding time, and heating rate on the formation of nascent tar during the polyvinylchloride pyrolysis, and proposed a new four-stage mechanism, including (1) dechlorination accompanied with inner cyclization, (2) aromatic chain scission, (3) release of quasi-3 rings or 3 rings group, and (4) release of 2 rings group. In general, PVC thermal degradation mainly consists of two stages: in the first stage, dehydrochlorination was the main reaction of PVC decomposition, leading to the release of HCl and the formation of conjugated polyene; in the second stage, aromatic hydrocarbons are formed from cyclization reactions of the conjugated polyene and also small molecule hydrocarbons are generated (Aracil et al., 2005; Jordan et al., 2001; Kim, 2001; Starnes, 2002; Yu et al., 2016).

Quantum chemistry theoretical methods is increasingly being applied to predict possible reaction pathways and to investigate the detailed thermal decomposition mechanism (Huang et al., 2014, 2016, 2018; Younker et al., 2012). The pyrolysis mechanism of PVC is complex and experimental studies are hard to get insight into the detailed decomposition mechanism. In the present study, the thermal decomposition processes of model compound of PVC (shown in Fig. 1) are investigated by using density functional theory methods M062X with the 6-31++G(d,p) basis set in order to expound the elimination of HCl and the formation of aromatic hydrocarbons. Due to computational "cost", we used a model compound of PVC (an oligomer containing 4 repeated units) instead of actual PVC polymers to investigate the pyrolysis mechanism of PVC. The model compound of PVC holds a chemical structure similar to the real PVC and is an intermediate appeared in the process of PVC pyrolysis, so the pyrolysis mechanism of model compound of PVC is similar to that of PVC and there is a similar product distribution during the pyrolysis of both PVC model and PVC.

2. Calculation methods

The M06-2X hybrid exchange-correlation functional (Zhao and Truhlar, 2008), which is confirmed to be more accurate than the method B3LYP in previous studies (Parthasarathi et al., 2011; Zhang et al., 2015), has been employed in all calculations. All calculations have been performed with the version of Gaussian 09 (Frisch et al., 2013) program package. The calculation details are the same as those in the literature (Huang et al., 2018).
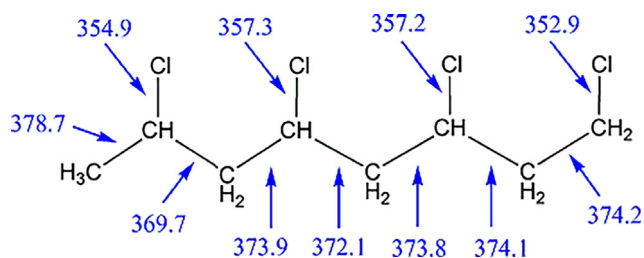

Fig. 1. Model compound of poly(vinyl chloride) (MPVC) and the BDE values marked in blue, calculated by using M06-2X/6-31++G(d,p) (kJ/mol).

3. Results and discussion

3.1. Bond dissociation energies

The values of the bond dissociation energies (BDEs) in MPVC, calculated by using M06-2X/6-31++G(d,p), are shown in Fig. 1. On the basis of these calculations, the weakest bond in PVC is the single bond between the chlorine atom and carbon atom (352.9 kJ/mol), and the average BDE value of branched-chain C—Cl bond for MPVC is 355.6 kJ/mol. Compared with C—Cl bond, the BDE of main-chain C—C bond is obviously higher, and the average BDE value of main-chain C—C bond for MPVC is 373.8 kJ/mol. Therefore, the cleavage of the branched-chain C—Cl bond is more likely to occur in the thermal decomposition of PVC.

Experimental results of the thermal decomposition of PVC (Castro et al., 2012; Gui et al., 2013; Yuan et al., 2014; Zhou et al., 2016) showed that the main products are HCl, aromatic hydrocarbons, small molecule hydrocarbons (for instance, methane, ethane, ethylene) and so on. Based on related experimental results, we propose various possible decomposition paths for the evolution of the main products, and the kinetic parameters in all paths were calculated.

3.2. Elimination mechanism of HCl

The first decomposition step in the PVC pyrolysis is the elimination of HCl. Schemes 1 and 2 describe seven proposed thermal decomposition paths for elimination mechanism of HCl and the kinetic schematic diagram is shown in Fig. 2. The optimized molecular structures in these decomposition paths are given in Figs. 3 and 4. In path (1), the elimination of HCl starts from the left end of the model compound **1**; in path (2), the elimination of HCl starts from the right end of the model compound **1**; in paths (3) and (4), the elimination of HCl starts from the middle of the model compound **1**; in path (5), the rupture of main chain C—C bond occurs, meanwhile there is a transfer of chlorine atom from one carbon atom to another carbon atom. Paths (6) and (7) describe the elimination of HCl for the model compound with branched-chain —CH₂CH₂Cl (or —CHClCH₃).

In reaction path (1), model compound **1** is decomposed into intermediate **2** and HCl via four-member ring transition state **TS₁** with an energy barrier of 214.9 kJ/mol through a concerted reaction, and the elimination reaction of HCl absorbs an energy of 92.4 kJ/mol; the intermediate **2** is decomposed into intermediate **3** and HCl via transition state TS₂ with an energy barrier of 207.4 kJ/mol, and the elimination reaction of HCl absorbs an energy of 61.3 kJ/mol; the intermediate **3** is decomposed into intermediate **4** and HCl via transition state TS₃ with an energy barrier of 203.5 kJ/mol, and the elimination reaction of HCl absorbs an energy of 61.7 kJ/mol; the intermediate **4** is decomposed into conjugated polyene **5** and HCl via transition state TS₄ with an energy barrier of 225.4 kJ/mol, and the elimination reaction of HCl absorbs an energy of 54.5 kJ/mol.

In reaction path (2), model compound **1** is decomposed into intermediate **6** and HCl via transition state **TS₅** with an energy barrier of 243.3 kJ/mol, and the elimination of HCl absorbs an energy of 81.6 kJ/mol; the intermediate **6** is decomposed into intermediate **7** and HCl via transition state **TS₆** with an energy barrier of 205.8 kJ/mol, and the elimination of HCl absorbs an energy of 57.2 kJ/mol; the intermediate **7** is decomposed into intermediate **8** and HCl via transition state **TS₇** with an energy barrier of 183.0 kJ/mol, and the elimination of HCl absorbs an energy of 60.9 kJ/mol; the intermediate **8** is decomposed into conjugated polyene **5** and HCl via transition state **TS₈** with an energy barrier of 177.8 kJ/mol, and the elimination of HCl absorbs an energy of 64.2 kJ/mol.