Density functional theory study on bond dissociation energy of polystyrene trimer model compound

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Abstract: The bond dissociation energy (BDE) of syndiotactic polystyrene(s-PS) was calculated by using four density functional theory methods, which were M062X, B3LYP, B3P86, BHandHLYP with different LANL2DZ, 6-31G(d), 6-31G(d, p), and 6-311++G(d, p) basis sets. The influence of these computational methods on the accuracy of the BDE of s-PS was analyzed. It was found that the BDE had a higher accuracy at B3P86/6-31G (d, p) level than other methods, and B3P86/6-31G (d, p) spent more less time to calculate the bond dissociation energy of s-PS, and the average of the C-C bonds’ BDE values calculated by B3P86/6-31G (d, p) is about 8.3 kJ/mol lower than the experimental value (310.0 kJ/mol), which is derived from the i-bond database. Besides, the bond dissociation energy values of the C-C bonds computed by M062X/LANL2DZ, B3LYP/6-31G(d), M062X/6-31G(d), B3LYP/LANL2DZ and BHandHLYP/6-311++G(d, p) methods were as follows: 330.8 kJ/mol, 345.3 kJ/mol, 283.2 kJ/mol, 267.6 kJ/mol, 267.4 kJ/mol. The calculation conclusion is drawn that different calculation methods with the same basis set have an obvious influence on the result of BDE values’ calculation. Finally, based on the calculation of bond dissociation energy of polystyrene, three possible reaction paths of polystyrene pyrolysis are designed to analyze the influence of bond dissociation energy on polystyrene pyrolysis.

1. Introduction
It is generally believed that polystyrene has three isomeric structures: syndiotactic, isotactic and atactic, which are composed of C-C bonds, C-H bonds and C-C_aromatic bonds. The reaction mechanism of free radicals is considered as the main mechanism in the pyrolysis process of polystyrene [1-4]. And the BDE value is a necessary parameter for the chemical properties of radical reactions to represent the strength of chemical bonds that is the energy required while the chemical bonds are breaking. The larger the BDE is that the less likely the chemical bond is to break [5, 6]. Polystyrene is a kind of high poly compound, which is polymerized by small molecules, its bond dissociation energy values are very important for the pyrolysis of polystyrene. The calculation of polystyrene’s BDE value is helpful to understand the pyrolysis mechanism of polystyrene. The BDE of s-PS is mainly calculated and studied in this paper because that it is the most stable structure for polystyrene molecules [7]. We use density functional theory methods, which are MO62X/LANL2DZ, MO62X/6-31G(d), B3LYP/6-31G(d), B3LYP/LANL2DZ, BHandHLYP/6-311++G(d, p), B3P86/6-31G(d, p) to calculate polystyrene trimer model compound’s C-H bonds, C-C bonds and C-C_aromatic bonds, and
analyze the polystyrene trimer model compounds’ BDE to compare the influence of the BDE values by these methods. The purpose is to find a more accurate method to calculate the BDE values of polystyrene, and to explore the influence of the bond dissociation energy values on the pyrolysis mechanism of polystyrene trimer model compounds.

2. Computational Method
The bond dissociation energy values were calculated by using Gaussian 09 program in this paper [8]. Four density functional theory methods, including M062X, B3LYP, B3P86 and BHandHLYP, and five different accuracy’s basis sets, such as LANL2DZ, 6-31G (d), 6-31G (d, p), 6-31++G (d, p) were selected to calculate and study the BDE of s-PS. The bond dissociation energy (BDE) of syndiotactic polystyrene(s-PS) was calculated by using the combination of the same method with different basis sets, different methods with the same basis set and different methods with different basis sets. M062X was a good hybrid functional in density functional theory method, which played a great role in the calculation of chemical bonds main groups [18]. B3LYP and B3P86 are all hybrid functional of Becke three-parameter, B3LYP uses the non-local correlation of LYP expression, B3LYP can relatively calculate molecular configuration, energy and frequency accurately. The non-local correlation of B3P86 is provided by Perdew 86 [9]. BHandHLYP is also mixed density functional. Some studies have shown that BHandHLYP is an unexceptionable method in all functional tests and it is one of the applicable methods to describe hydrogen bonding systems. Different density functional methods use different correlative exchange function. As a result, the calculation results were different [10, 11]. The calculation formula of bond dissociation energy for each major bond splitting reaction is [12]:

\[ E_{B}(R-X) = E(R) + E_{ZP}(R) + E(X) + E_{ZP}(X) - E(RX) - E_{ZP}(RX) \]

In this formula, \( E_B \) represents the bond dissociation energy when zero correction is taken into account, \( E \) is the molecular energy, and \( E_{ZP} \) is the zero correction energy.

Figure 1. Molecular structure of syndiotactic polystyrene.

3. Results and Discussion

3.1. The energy dissociation of the C-C bonds
Figure 1 shows the structure of s-PS, which consists of main-chain C-C bonds and three alternating benzene rings. The experimental values of BDE of C-C bond, C-H bond and C-C aromatic of s-PS are 310.0 kJ/mol, 351.5 kJ/mol and 415.1 kJ/mol respectively, Table 1 lists the values of the BDE of the C-C bonds calculated by different methods. The average value of the BDE obtained by M062X/6-31G (d) is 345.3 kJ/mol, and the average values of the BDE calculated by M062X/LANL2DZ is 330.8 kJ/mol, its deviations with the experimental value are respectively 35.3 kJ/mol and 20.8 kJ/mol. The computational results of M062X/6-31G (d) and M062X/LANL2DZ method have a large deviation with the experimental value, and the error of M062X/6-31G (d) is larger than that of M062X/LANL2DZ method. The average BDE value of C-C bonds of syndiotactic polystyrenet at B3LYP/6-31G(d) and B3LYP/LANL2DZ level are respectively 283.2 kJ/mol and 267.6 kJ/mol, and its errors with the experimental values are respectively 26.2 kJ/mol and 42.4 kJ/mol. By comparing the results calculated by the combination of the above methods and basis groups, it is concluded that LANL2DZ basis set is relatively accuracy than the basis set 6-31G (d) when M062X method is used for C-C bonds calculation. The LANL2DZ basis set is not as accurate as the 6-31G (d) when the method B3LYP is used to calculate the BDE of C-C bonds. For LANL2DZ basis set, the values
obtained by M062X method are more accurate than the result obtained by B3LYP method. The average values calculated by BHandHLYP/6-311++G (d, p) is 267.4 kJ/mol, it is about 42.6 kJ/mol lower than the experimental value. The calculated result by B3P86/6-31G (d, p) method is 301.7 kJ/mol, its calculation time is shorter than above five methods, and the error value is 8.3 kJ/mol, which is the most similar to the experimental value.

From the above discussion, the C–C bonds’ BDE values are calculated by using the combination of the same method with different basis sets, and the combinations of the same set with different methods. The results obtained by M062X method, B3LYP method and BHandHLYP/6-311++G (d, p) have a great error with the experimental values. B3P86/6-31G (d, p) method is the closest to the experimental value and relatively accurate.

Table 1. The values of C–C bond dissociation energy (kJ/mol).

| C–C bonds | M062X/6-31G(d) | M062X/LANL2DZ | B3LYP/6-31G(d) | B3LYP/LANL2DZ | B3P86/6-31G(d, p) | BHandHLYP/6-311++G(d, p) |
|-----------|----------------|---------------|----------------|---------------|-------------------|--------------------------|
| C1–C2     | 347.1          | 332.4         | 288.5          | 272.1         | 306.5             | 270.3                    |
| C2–C3     | 348.2          | 334.4         | 278.9          | 264.9         | 298.2             | 264.6                    |
| C3–C4     | 345.7          | 332.5         | 277.6          | 264.0         | 297.6             | 264.2                    |
| C4–C5     | 340.3          | 326.7         | 276.7          | 261.6         | 294.7             | 262.7                    |
| C5–C6     | 345.2          | 327.9         | 294.1          | 275.2         | 311.4             | 275.1                    |
| Average   | 345.3          | 330.8         | 283.2          | 267.6         | 301.7             | 267.4                    |

3.2. The energy dissociation of C–C aromatic bonds

The following table 2 marks the required values of C–C aromatic bonds calculated by M062X/6-31G (d), M062X/LANL2DZ, B3LYP/6-31G (d), B3LYP/LANL2DZ and B3P86/6-31G (d, p) methods. The calculated results of C–C aromatic are respectively 435.8 kJ/mol and 433.0 kJ/mol by using M062X/6-31G (d) and M062X/LANL2DZ methods, and the errors between them with the experimental values are respectively as high as 20.7 kJ/mol and 17.9 kJ/mol. This calculation result indicates that M062X/6-31G (d) method isn’t too different from the result of the M062X/LANL2DZ, but all the calculation values are more higher than experimental value. The average BDE values of C–C aromatic bonds calculated by B3LYP/6-31G (d) and B3LYP/LANL2DZ method are 388.7 kJ/mol and 384.2 kJ/mol respectively, and calculated results are respectively about 26.4 kJ/mol and 30.9 kJ/mol lower than the experimental value. The average BDE values at BHandHLYP/6-311++G (d, p) level has a highest error to experimental value, which is 38.3 kJ/mol. A relatively accurate calculation results can acquired by B3P86/6-31G (d, p), the average value is 406.4 kJ/mol, which is the most similar to experimental value, it is only 8.7 kJ/mol lower than experimental value.

As for M062X and B3LYP methods, the results obtained by M062X/ 6-31G (d) and M062X/LANL2DZ methods are semblable, the result obtained by B3LYP/ 6-31G(d) is similar to the result of B3LYP/LANL2DZ method, But the C–C aromatic bonds BDE values obtained by these four methods are very different from the experimental values. The average values obtained by BHandHLYP/6-311++G (d, p) has a largest deviation. The results show that those computing methods of M062X/6-31G (d), M062X/LANL2DZ, B3LYP/6-31G (d), B3LYP/LANL2D and BHandHLYP/6-311++G (d, p) are not suitable for C–C aromatic bonds dissociation energy’s calculation. B3P86/6-31G (d, p) is the most accurate calculation way, which is more suitable for the calculation of polystyrene C–C aromatic bond dissociation energy.
Table 2. The values of C-C aromatic bond dissociation energy (kJ/mol).

| Methods                  | C1-C aromatic | C2-C aromatic | C3-C aromatic | Average value |
|--------------------------|---------------|---------------|---------------|---------------|
| M062X/6-31G(d)           | 443.6         | 429.1         | 434.6         | 435.8         |
| M062X/LANL2DZ            | 438.6         | 428.8         | 431.5         | 433.0         |
| B3LYP/6-31G(d)           | 399.9         | 384.1         | 382.0         | 388.7         |
| B3LYP/LANL2DZ            | 392.1         | 382.2         | 378.3         | 384.2         |
| B3P86/6-31G(d, p)        | 415.8         | 403.6         | 399.7         | 406.4         |
| BHandHLYP/6-311++G(d, p) | 384.6         | 374.3         | 371.6         | 376.8         |

3.3. The energy dissociation of the C-H bonds

Table 3 shows the values of the bond dissociation energy of C-H bonds. Through calculation, the average value calculated by M062X/6-31G (d) was 397.6 kJ/mol, and the error with the experimental value is 46.1 kJ/mol. The C-H bonds' average BDE values calculated by M062X/LANL2DZ method is 397.0 kJ/mol, its error with the experimental value is 45.5 kJ/mol. The average bond dissociation energy value calculated by B3LYP/6-31G (d) method was 385.4 kJ/mol, its error of BDE value with experimental value as 33.9 kJ/mol. The value calculated by B3LYP/LANL2DZ method is 383.9 kJ/mol, it is about 32.4 kJ/mol higher than experimental value. The average bond dissociation energy of C-H bonds calculated by B3P86/6-31G (d, p) method was 398.6 kJ/mol, the error with the experimental value is 47.1 kJ/mol. The average dissociation energy of C-H bonds obtained by BHandHLYP/6-311++G (d, p) method was 313.7 kJ/mol, and the error with the experimental value is 37.8 kJ/mol.

By comparing the results obtained by each method to experimental value. It is concluded that the values calculated by M062X/6-31G (d) and M062X/LANL2DZ methods are basically the same for C-H bonds' BDE, the values obtained by B3LYP/6-31G (d) and B3LYP/LANL2DZ are not significantly different. But all of them are quite different from the experimental values. The result computed by M062X/6-31G (d) is more accurate than B3LYP/6-31G (d) method. Comparing M062X/LANL2DZ with B3LYP/LANL2DZ, the M062X/LANL2DZ method is not applicable to calculate C-H bonds' BDE. The results obtained by the combination of these methods with the same basis set show that different methods with the same basis set have a great influence on the calculation of C-H bonds' BDE. The values calculated by BHandHLYP/6-311++G (d, p) is about 37.8 lower than experimental value. In summary, in the calculation of C-H bonds dissociation energy, the selection of 6-31G (d) basis set and LANL2DZ basis set has a little influence on the calculation results. The error of B3LYP method is smaller than that all of other methods, but the result is not ideal to calculate the C-H bond dissociation energy.

Table 3. The values of bond dissociation energy of C-H bonds (kJ/mol).

| Methods                  | C1-H          | C2-H          | C3-H          | C4-H          | C5-H          | C6-H          | Average value |
|--------------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| M062X/6-31G(d)           | 375.9         | 414.8         | 391.0         | 412.8         | 364.4         | 426.7         | 397.6         |
| M062X/LANL2DZ            | 374.6         | 413.4         | 393.1         | 412.0         | 364.6         | 424.5         | 397.0         |
| B3LYP/6-31G(d)           | 354.1         | 403.0         | 385.1         | 402.2         | 348.9         | 419.0         | 385.4         |
| B3LYP/LANL2DZ            | 352.8         | 402.4         | 381.7         | 402.4         | 347.5         | 416.5         | 383.9         |
| B3P86/6-31G(d, p)        | 369.1         | 416.3         | 396.2         | 416.2         | 362.0         | 431.5         | 398.6         |
| BHandHLYP/6-311++G(d, p) | 348.0         | 395.8         | 395.1         | 408.1         | 384.3         | 346.1         | 313.7         |

3.4. Analysis on the formation mechanism of polystyrene pyrolysis products

Liu, X.X., et al. [13] concluded that styrene, ethylbenzene, toluene, alpha-methyl styrene products and
so on are the main products of polystyrene pyrolysis reaction. This part mainly proposes three possible reaction paths to the formation mechanism of styrene dimer, styrene, ethylbenzene, alpha-methyl styrene products during the pyrolysis of polystyrene. According to the density functional theory method in Gaussian 09 (B3P86/6-31G (d, p)), reaction kinetics parameters and thermodynamic parameters are calculated and the formation mechanism of main products is studied in the pyrolysis reaction process. Figure 2 describes three possible reaction paths in the pyrolysis process of polystyrene, it can reflect the evolution process of each product generated by PS pyrolysis. Figure 3 depicts the energy barrier diagram of each reaction stage in the three reaction paths, which can well show the kinetic principles of the reaction process.

In the reaction of path 1, the styrene monomer 2 and free radical 3 are generated by breaking of the C4-C5 bond of polystyrene free radical 1 under the transition state TS1. In this process, there is 82.6 kJ/mol heat absorbed, and the reaction energy barrier is 162.3 kJ/mol. The free radicals 3 generate styrene monomer 2 and a free radical 4 by TS2 after the C2-C3 bond’s breaking. It absorbs 82.6 kJ/mol quantity of heat, and the reaction energy barrier is 118.6 kJ/mol in this process. Radical 4 get one hydrogen to form ethylbenzene 5, which releases 367.2 kJ/mol energy. Or generates styrene monomer 2 by dehydrogenation, and absorbs 218.5 kJ/mol energy.

In the reaction of Path 2, the reaction mechanism of styrene dimer generated by polystyrene pyrolysis is mainly 1, 3 hydrogen transfer within polystyrene molecules. The C1’s H of the free radical 1 is transferred to C3 to form free radical 6 through the transition state TS3, it absorbs 27.1 kJ/mol heat, and the reaction energy barrier is 165.2 kJ/mol during the process, which is so low. The C2-C3 bond of the free radical 6 is broken and the styrene dimer 7 and free radical 4 were generated through the transitional state TS4. This process absorbs heat of 27.1 kJ/mol, and the reaction energy barrier is 165.6 kJ/mol. Free radical 4 releases 367.3 kJ/mol heat by getting a hydrogen to form ethylbenzene 5, or by dehydrogenating to make styrene monomer 2, which absorbs 218.4 kJ/mol heat. The reaction of this path not only produces styrene dimer, but also styrene monomer and ethylbenzene. This path makes the reaction reactive fully.

In the reaction path Path 3, the main reaction mechanism of polystyrene pyrolysis to produce alpha-methyl styrene is 1, 2 hydrogen transfer in polystyrene molecules. The C1’s H of the free radical 1 is transferred to the position of C2 by transition state TS5 to form radical 8. In this process, 47.3 kJ/mol is absorbed, and the energy barrier of this reaction is 182.7 kJ/mol. The C3-C4 bond of Free radical 8 is broken, and the product 9 and free radical 10 are formed under the function of the transition state TS6. This process absorbed 47.3 kJ/mol of heat, and the energy barrier of this reaction is 180.8 kJ/mol. Radical 10 generates alpha-methyl styrene monomer 11 by removing one hydrogen, which absorbs 146.4 kJ/mol of heat.

By comparing and analyzing the energy barrier values of each path in figure 3, the path 1 has the...
lowest reaction rate control step energy barrier to generate styrene monomer. It can draw a conclusion that the reaction is easier to carry out, so a large number of styrene monomers can be generated, it is consistent with the findings [16]. In addition, in the three reaction paths, the pyrolysis reaction of polystyrene mainly involves the fracture of C-C bonds on the main chain of polystyrene molecule, free radical reaction, dehydrogenation reaction and hydrogen transfer. In the calculation of the bond dissociation energy of C-C, C-Caromatic and C-H bonds, the values of C-C and C-H bonds are generally lower than the C-Caromatic bonds. The reaction is not easy to form benzene rings, which is consistent with the calculation results [13].

![Figure 3. Reaction energy barrier diagrams of PS pyrolysis path1, 2, 3.](image)

4. Conclusion
Bond dissociation energy is an important parameter for radical reaction. It’s calculated by using the combination of the same density functional method with different base sets, different methods with the same basis set. According to the calculative results, the following conclusions are drawn:

1. The methods of M062X/6-31G (d), M062X/LANL2DZ, B3LYP/6-31G (d), B3LYP/LANL2DZ and BHandHLYP/6-311++G (d, p) has a large error in polystyrene BDEs’ calculation. And the combination of different basis sets with the same method has little influence on the calculation results, while the same basis set with different methods has certain influence on the calculation results.

2. The method of B3P86/6-31G (d, p) has a large error in C-H bonds’ calculation. But generally speaking, it is relatively accurate for calculating the BDEs of polystyrene, and the calculation time is shorter than other methods. It is feasible to utilize in the calculation of t polystyrene’s BDEs.

3. The pyrolysis reaction of polystyrene mainly involves the fracture of C-C bonds, free radical reaction, dehydrogenation reaction and hydrogen. In the calculation of BDEs, the values of C-C and C-H bonds are generally lower than the C-Caromatic bonds. The results show that the smaller the bond
dissociation energy, the more likely the bond is to break, the easier the reaction is to carry out.

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