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RESEARCH PAPER

Theoretical study on the effect of the substituent groups on the homolysis of the ether bond in lignin trimer model compounds

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Abstract: The homolytic bond dissociation energies (BDEs) of C_α–O and C_β–O bonds in 27 lignin trimer model compounds were calculated by employing density functional theory methods at M062X level with 6–31++G(d,p) basis set; the effects of various substituent groups (CH_3, CH_2OH and OCH_3) at different positions on the BDEs of C_α–O and C_β–O bonds were investigated. The results indicated that a single methoxyl group at R_2 or R_3 has a minor influence on the BDE of C_β–O bond, whereas two methoxyl groups at R_2 and R_3 lead to an obvious decrease in the BDE of C_β–O bond. The decrement in the BDE of C_β–O bond from the methoxyl groups at R_2 and R_3 can be enhanced by the methoxyl groups at R_4 and R_5, but is hardly influenced by the substituent groups at R_1. Meanwhile, the BDE of C_α–O bond is gradually reduced when the H atoms at R_4 and R_5 are successively substituted with methoxyl groups; the decrement in the BDE of C_α–O bond from the methoxyl groups at R_4 and R_5 can be strengthened by the methoxyl groups at R_2 and R_3. Furthermore, the methyl and hydroxymethyl groups at R_1 can gradually increase the BDE of C_α–O bond and this effect is weakened when the H atoms at R_2 and R_3 are successively substituted with methoxyl groups. The methyl group at R_1 has little influence on the BDE of C_β–O bond, which is however dramatically increased by the hydroxymethyl group at R_1.

Key words: lignin trimer model compound; substituent group; homolysis; bond dissociation energy; density functional theory

Pyrolysis is one of the most promising technologies for the efficient utilization of biomass[1–5]. As one of the three primary components of biomass, lignin is a complex, amorphous and three-dimensional polymer, arising from the random polymerization of three primary phenylpropanoid subunits, viz., *p*-hydroxyl phenylpropane, guaiacylpropane and syringylpropane, which are bonded together via several C–O and C–C inter-unit linkages[6,7]. Among these linkages in lignin, *β*–O–4 ether is the dominant one which accounts for more than half of all linkages[8], whilst *α*–O–4 linkage is the second most abundant ether linkage[9]. The lignin structure is complex and varies with the biomass species; therefore, appropriate lignin model compounds are usually employed to study the mechanism of lignin pyrolysis. Previous studies based on density functional theory (DFT) calculations have verified that the homolytic decomposition was the predominant reaction in the initial stage for lignin pyrolysis, in which the homolysis of *α*–O–4 and *β*–O–4 bonds took place quite easily[10–12]. The substituents on both the aromatic and alkyl groups, for example, the methoxyl and hydroxyl substituents, exhibited remarkable effects on the bond dissociation energies (BDEs) of *α*–O–4 and *β*–O–4 bonds, influencing the subsequent reactions and the distribution of pyrolytic products[9,13–16]. However, previous studies mainly focused on the lignin dimer model compounds with only one linkage, whereas very limited attentions were paid on the lignin model compounds containing two or more linkages[17].

Hence, in this work, the homolytic BDEs of C_α–O and C_β–O bonds in 27 lignin trimer model compounds were calculated, which contained both the *α*–O–4 and *β*–O–4 linkages substituted with methyl, hydroxymethyl and methoxyl groups, as shown in Figure 1, to investigate the effects of various substituents at different positions on the BDEs of the ether bonds.

1 Calculation methods

All calculations were performed by using Gaussian 09 suit of programs[18]. The equilibrium geometries of reactants and radicals formed from the homolytic process were optimized

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by using DFT/M062X method with the 6–31++G(d,p) basis set. Standard thermodynamic parameters were obtained by the vibrational frequency calculations at the same theoretical level under 298 K and 101325 Pa. The M062X method has been newly developed and employed in the theoretical studies of lignin pyrolysis mechanism[19–21], which proved to be more accurate than the B3LYP method. The lignin trimer can adopt diverse spatial configurations via rotations around its covalent bonds. Therefore, it is essential to give multiple initial configurations during the optimization process to obtain the lowest energy configuration. All the optimized structures had no imaginary frequency, which was certified through frequency analysis; their energies were obtained after zero-point energy (ZPE) correction[22]. The BDEs of the major ether bonds in lignin trimer model compounds were calculated as[23]:

$$E_0(A–B)=E(A\cdot) + E_{ZP}(A\cdot) + E(B\cdot) + E_{ZP}(B\cdot) - E(AB) - E_{ZP}(AB) \qquad (1)$$

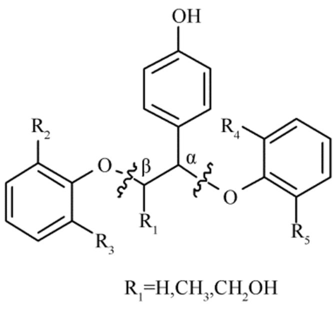
where E_0, E, and E_{ZP} are the bond dissociation energy (including the ZPE), the molecular energy and the zero-point energy, respectively.

2 Results and discussion

2.1 Effects of the methoxyl substituents at R₂ and R₃ on the BDEs of C_β–O bonds

The model compounds are grouped in terms of the same substituents at R_1 and $R_{4,5}$. The BDEs of C_β–O bonds are listed in Table 1 in the order of none, one and two methoxyl substituents at $R_{2,3}$. Meanwhile, the differences in BDEs (ΔBDEs) between two adjacent model compounds in Table 1 are also calculated.

In group A1 ($R_{1,4,5}$ = H), when H atom at R_2 of Model Compound 1 (MC1) is substituted by the methoxyl group, the BDE of C_β–O bond is increased from 294.3 to 294.9 kJ/mol (MC2), with an increment of 0.6 kJ/mol. When H atom at R_3 is further substituted with the methoxyl group, the BDE is decreased by 8.9 to 286.0 kJ/mol (MC3).



R_1=H,CH_3,CH_2OH
R_{2-5}=H,OCH_3

Fig. 1 Spatial structure and major homolytic cleavage ways of lignin trimer model compound

This suggests that single methoxyl substituent at R_2 or R_3 has a minor effect on the BDE of C_β–O bond, whereas two methoxyl substituents at R_2 and R_3 may obviously reduce the BDE of C_β–O bond. The weakening of C_β–O bond can be attributed to the steric hindrance induced by the methoxyl substituents at R_2 and R_3, which agrees well with the experimental results obtained by Britt et al[14]. Through calculating the BDEs of C_β–O bonds of methoxyl-substituted lignin dimer model compounds, however, Beste et al[15] found that a methoxyl substituent at R_2 or R_3 could reduce the BDE of C_β–O bond by 22.9 kJ/mol and an additional methoxyl substituent could further decrease the BDE by 14.6 kJ/mol. As the lignin model compounds used in this work is different from those used by Beste et al[15], current results may suggest that the phenoxyl at C_α position of the lignin trimer model compound has a great influence on the BDE of C_β–O bond.

In group A2 ($R_{1,5}$ = H, R_4 = OCH_3), the BDEs of C_β–O bonds are 308.6, 291.7 and 271.7 kJ/mol for MC4, MC8 and MC10, respectively; ΔBDEs are –16.9 and –20.0 kJ/mol, for MC4 to MC8 and MC8 and MC10, respectively. In group A3 (R_1 = H, $R_{4,5}$ = OCH_3), the BDEs are 304.6, 279.8 and 260.3 kJ/mol for MC5, MC9 and MC11, respectively, with the ΔBDEs of –24.8 (MC5 to MC9) and –19.5 kJ/mol (MC9 to MC10). In comparison with group A1, the effect of the methoxyl substituents at R_2 and R_3 on the BDE of C_β–O bond is dramatically enhanced in group A2 and A3; the absolute values of ΔBDEs exceed 16 kJ/mol. It indicates that the methoxyl substituents at R_4 and R_5 can strengthen the increment in the BDE of C_β–O bond from the methoxyl substituents at R_2 and R_3, which are further illustrated by comparing the ΔBDEs in group A4 with A6 and group A7 with A9.

In group A4 (R_1 = CH_3, $R_{4,5}$ = H), the BDEs of C_β–O bonds are 294.9, 293.9 and 286.8 kJ/mol for MC6, MC14 and MC15, respectively, with the ΔBDEs of –1.0 (MC6 to MC14) and –7.1 kJ/mol (MC14 to MC15). In group A7 (R_1 = CH_2OH, $R_{4,5}$ = H), the BDEs are 302.3, 303.0 and 296.8 kJ/mol for MC7, MC12 and MC13, respectively, with the ΔBDEs of –0.7 (MC7 to MC12) and –6.2 kJ/mol (MC12 to MC13). The ΔBDEs in group A4 and A7 are approximate to those in group A1, indicating that the methyl and hydroxymethyl substituents at R_1 have little effect on the alteration of BDE of C_β–O bond induced by the methoxyl substituents at R_2 and R_3.

2.2 Effects of the methoxyl substituents at R₄ and R₅ on the BDEs of C_α–O bonds

The model compounds are grouped in terms of the same substituents at $R_{1–3}$. The BDEs of C_α–O bonds are listed in Table 2 in the order of none, one and two methoxyl substituents at $R_{4,5}$. Meanwhile, the ΔBDEs between two adjacent model compounds are calculated in Table 2.