

Addendum to “Comparison of ReaxFF, DFTB, and DFT for Phenolic Pyrolysis. 1. Molecular Dynamics Simulations” and “Comparison of ReaxFF, DFTB, and DFT for Phenolic Pyrolysis. 2. Elementary Reaction Paths”

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We recently published two related manuscripts on phenolic pyrolysis, denoted parts 1 and 2. As stated in part 2, the DFT B3LYP geometries were used for all levels of theory. On the basis of previous work using DFT and traditional methods, we expected this approximation to introduce negligibly small errors. Recently we became aware that the ReaxFF geometries can differ significantly from the B3LYP results.¹ We have therefore optimized the geometries for each level of theory, excluding the CCSD(T) method where the B3LYP geometries are used. The methods are as described in parts 1 and 2, except for the geometric optimization. As expected, the PW91 and DFTB results were only slightly changed by optimizing the geometry. Unlike the other methods, the ReaxFF values changed significantly with geometry optimization.

Table 1, which is analogous to Table 1 in part 1, shows that ReaxFF bond energies are now in better agreement with the CCSD(T) than those obtained using the DFTB method. Table 2 updates Table 2 in part 1. Comparison shows that ReaxFF description of some C–C bond energies improves when the relaxed geometries are used. For all five C–C bond breaking reactions, ReaxFF underestimates the bond energy and DFTB overestimates. Finally, a mistake in part 1 has been found regarding the bond lifetime criterion on page 11117, first column, fourth paragraph: “50 or more femtoseconds” should be replaced by “200 or more femtoseconds”. We find that a 52 fs lifetime decreases atomic hydrogen populations by approximately a factor of 2 and increases the char percentage by 10–30% for all energy models. Changes to other species populations are less significant.

Tables 3–7 update Tables 1–5 in part 2. As noted above, performing ReaxFF calculations at the ReaxFF optimized geometries reduces the difference between the CCSD(T) and ReaxFF energies. Unfortunately, we have been unable to optimize the transition states using the ReaxFF; however, we suspect that the barrier heights will also improve on the basis of our approximate transition state calculations.

The effects of geometry relaxation are summarized in Table 7 by the average and maximum deviations from the CCSD(T) energies. Comparison of the fixed and relaxed geometry ReaxFF results in this table shows that the difference from the CCSD(T) for the bond and reaction energies is reduced by approximately a factor of 2. Geometry relaxation brings the ReaxFF energies into closer agreement with CCSD(T) than the DFTB energies.

Table 1. C₆H₅OH Bond Energies Calculated Using DFT, CCSD(T), DFTB (mio-1-1 and pbc-0-3 parameter sets), and ReaxFF^a

| bond | DFT | CCSD(T) cc-pVTZ | DFTB | | ReaxFF |
|--------|-------|--------------------|-------|-------|--------|
| | | | mio | pbc | |
| O–H | 91.1 | 95.3 | 125.5 | 125.0 | 102.6 |
| C–OH | 124.0 | 115.9 | 148.4 | 154.0 | 97.4 |
| C–H(1) | 116.7 | 121.0 | 150.6 | 145.1 | 116.9 |
| C–H(2) | 116.4 | 120.3 | 150.5 | 145.0 | 112.5 |
| C–H(3) | 117.8 | 121.6 | 151.9 | 146.4 | 116.4 |
| C–H(4) | 116.5 | 120.3 | 151.0 | 145.5 | 113.3 |
| C–H(5) | 118.4 | 122.5 | 151.4 | 145.9 | 117.3 |

^aEnergy units are kcal/mol. Due to the high computational cost, CCSD(T) calculations are performed at relaxed geometries from DFT.

Table 2. C–C Bond Energies for the Isolated Molecules C₁₃H₁₂O₂ and C₁₃H₁₃O₂C₁₃H₁₃O₂ Using DFT, DFTB (mio-1-1 and pbc-0-3 parameter sets), and ReaxFF^a

| reaction label | DFT | DFTB | | ReaxFF |
|----------------|-------|-------|-------|--------|
| | | mio | pbc | |
| i | 90.6 | 112.2 | 114.4 | 79.5 |
| ii | 141.8 | 144.2 | 146.0 | 92.1 |
| iii | 47.9 | 47.3 | 55.6 | 47.1 |
| iv | 143.9 | 160.7 | 162.8 | 103.0 |
| v | 57.0 | 68.9 | 71.2 | 46.3 |

^aFive different C–C bond breaking reactions that might occur in pyrolysis are labeled (i, ii, iii, iv, and v). The energy unit is kcal/mol. DFT energies are lowest, suggesting the least stable carbon rings. A difference in C–C bond energy (e.g., between ii and iii) is observed when a nearby hydrogen atom is allowed to transfer in addition to C–C bond breakage.

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Table 3. C₆H₅OH Bond Energies (kcal/mol) at the DFT, CCSD(T), DFTB, and ReaxFF Levels of Theory^a

| bond | DFT | | | CCSD(T) | | | DFTB | | ReaxFF | |
|--------|-----------|-------|-------|---------|---------|---------|-------|-------|--------|-------|
| | B3LYP+zpe | B3LYP | PW91 | 6-31G** | cc-pVTZ | cc-pVQZ | mio | pbc | fixed | relx |
| O–H | 81.3 | 89.6 | 89.1 | 90.1 | 95.3 | 96.4 | 125.4 | 124.9 | 110.3 | 102.6 |
| C–OH | 107.9 | 113.4 | 121.1 | 112.1 | 115.9 | 117.1 | 148.4 | 154.0 | 115.4 | 97.4 |
| C–H(1) | 110.8 | 118.9 | 116.9 | 118.7 | 121.0 | 121.7 | 150.8 | 145.3 | 156.5 | 116.9 |
| C–H(2) | 110.1 | 118.3 | 116.4 | 118.0 | 120.3 | 121.1 | 150.7 | 145.3 | 142.7 | 112.5 |
| C–H(3) | 111.4 | 119.6 | 117.8 | 119.2 | 121.6 | 122.3 | 151.9 | 146.5 | 145.8 | 116.4 |
| C–H(4) | 110.1 | 118.4 | 116.5 | 118.0 | 120.3 | 121.1 | 151.1 | 145.6 | 143.5 | 113.3 |
| C–H(5) | 112.5 | 120.6 | 118.7 | 120.4 | 122.5 | 123.2 | 151.7 | 146.2 | 158.2 | 117.3 |

^aThe C–H bonds are defined in Figure 2 in part 2. The inclusion of zero-point energies is denoted with “+zpe”.Table 4. Energetics (kcal/mol) for CO Forming Reaction at Several Levels of Theory^a

| reaction path | DFT | | | CCSD(T) | | DFTB | | ReaxFF | |
|---------------|-----------|-------|-------|---------|---------|-------|-------|--------|-------|
| | B3LYP+zpe | B3LYP | PW91 | 6-31G** | cc-pVTZ | mio | pbc | fixed | relx |
| 1.1 | 65.1 | 69.3 | 61.0 | 72.7 | | 72.0 | 80.6 | 151.8 | |
| 1.2 | 16.8 | 17.6 | 17.4 | 18.4 | | 21.6 | 26.6 | 55.0 | 31.4 |
| 1.3 | 51.6 | 54.6 | 50.3 | 58.0 | | 50.3 | 58.4 | 102.0 | |
| 1.4 | 44.7 | 47.6 | 47.9 | 48.3 | | 50.1 | 58.3 | 98.7 | 49.8 |
| 1.5 | 114.2 | 120.5 | 124.1 | 118.7 | | 105.3 | 115.9 | 131.6 | |
| 1.6 | 32.2 | 36.6 | 43.0 | 28.1 | | 25.9 | 34.2 | 45.6 | 45.6 |
| 2.1 | 81.3 | 89.6 | 89.1 | 95.3 | | 125.4 | 124.9 | 110.3 | 102.6 |
| 2.2 | 132.8 | 143.5 | 135.7 | 145.8 | | 183.9 | 176.7 | 166.9 | |
| 2.3 | 129.7 | 139.7 | 133.1 | 140.4 | | 177.2 | 174.7 | 175.8 | 138.3 |
| 2.4 | 137.7 | 148.2 | 139.5 | 150.3 | | 190.4 | 184.7 | 171.9 | |
| 2.5 | 120.1 | 129.8 | 127.8 | 126.2 | | 158.8 | 158.7 | 151.8 | |
| 2.6 | 124.4 | 135.5 | 133.7 | 132.9 | | 153.1 | 149.4 | 145.0 | |
| 2.7 | 110.7 | 124.4 | 130.3 | 118.1 | | 144.2 | 147.1 | 99.0 | 99.2 |
| 3.1 | 143.0 | 148.7 | 149.3 | 152.1 | | 160.5 | 162.4 | 159.6 | |
| 3.2 | 111.6 | 116.8 | 119.1 | 119.7 | | 138.0 | 145.7 | 143.3 | |
| 3.3 | 116.8 | 123.7 | 125.8 | 128.0 | | 136.4 | 146.7 | 150.6 | |
| 3.4 | 101.4 | 109.5 | 119.3 | 108.1 | | 124.3 | 134.9 | 109.3 | 96.6 |
| 4.1 | −25.9 | −31.4 | −30.9 | −26.7 | −28.0 | −49.3 | −44.1 | −45.9 | −48.2 |
| 4.2 | 26.2 | 23.8 | 20.3 | 30.2 | 29.6 | 12.9 | 26.3 | 17.9 | |
| 4.3 | 7.4 | 1.9 | 2.6 | 3.9 | 7.0 | −5.9 | 4.3 | 14.3 | −5.3 |
| 4.4 | 18.4 | 14.9 | 13.5 | 20.4 | 21.4 | 2.9 | 9.6 | 19.4 | |
| 4.5 | −5.7 | −9.4 | −6.3 | −2.5 | −0.8 | −13.6 | −0.1 | 9.6 | −16.9 |
| 4.6 | 26.6 | 24.4 | 24.1 | 27.3 | 28.9 | 14.3 | 27.6 | 41.5 | |
| 4.7 | −15.3 | −19.7 | −18.1 | −20.4 | −18.0 | −30.8 | −19.9 | 1.0 | −21.9 |
| 4.8 | 15.6 | 14.2 | 13.7 | 16.7 | 18.0 | −5.1 | 8.4 | 26.8 | |
| 4.9 | 10.8 | 10.2 | 15.0 | 8.7 | 10.1 | 0.2 | 13.8 | 23.5 | 8.4 |
| 4.10 | 32.2 | 36.6 | 43.0 | 24.3 | 28.1 | 26.0 | 34.2 | 45.5 | 45.6 |

^aThe inclusion of zero-point energies is denoted with “+zpe”.Table 5. Comparison of the H₂ Reaction Path Energetics (kcal/mol) Computed Using DFT, CCSD(T), DFTB, and ReaxFF^a

| reaction path | DFT | | | CCSD(T) | | DFTB | | ReaxFF | |
|-----------------------|-----------|-------|------|---------|---------|------|------|--------|------|
| | B3LYP+zpe | B3LYP | PW91 | 6-31G** | cc-pVTZ | mio | pbc | fixed | relx |
| CH ₃ Model | | | | | | | | | |
| barrier (TS) | 63.7 | 68.9 | 62.4 | 75.8 | 74.8 | 93.5 | 89.0 | 108.2 | |
| products | 38.7 | 47.1 | 49.2 | 45.9 | 49.5 | 87.1 | 81.4 | 83.7 | 66.3 |
| Nonplanar Model | | | | | | | | | |
| barrier (TS) | 56.0 | 61.4 | 54.1 | 70.1 | | 83.4 | 79.1 | 103.2 | |
| products | 32.4 | 40.6 | 41.5 | 42.9 | | 79.5 | 73.8 | 76.7 | 61.2 |

^aThe B3LYP structures are shown in part 2. The inclusion of zero-point energies is denoted with “+zpe”.

Table 6. H₂O Reaction Path Energetics (kcal/mol) at the DFT, CCSD(T), DFTB, and ReaxFF Levels of Theory^a

| reaction path | DFT | | | CCSD(T) | | | DFTB | | ReaxFF | |
|--|-----------|-------|-------|---------|---------|---------|------|------|--------|------|
| | B3LYP+zpe | B3LYP | PW91 | 6-31G** | cc-pVTZ | cc-pVQZ | mio | pbc | fixed | relx |
| Interchain Model | | | | | | | | | | |
| barrier (TS) | 85.4 | 87.1 | 75.2 | | | | 77.3 | 75.4 | 60.1 | |
| product | 5.6 | 7.4 | 7.8 | | | | −3.1 | −5.6 | −13.2 | 6.1 |
| CH ₃ Model | | | | | | | | | | |
| barrier (TS) | 95.4 | 97.8 | 93.4 | 104.0 | 95.1 | 94.6 | 82.2 | 78.3 | 53.8 | |
| product | 99.8 | 105.4 | 106.7 | 101.8 | 99.1 | 98.4 | 98.4 | 98.3 | 112.4 | 81.5 |
| Nonplanar Model: Bridge H to OH Transfer | | | | | | | | | | |
| 5.1 | 86.7 | 88.5 | 83.3 | 96.5 | 89.0 | | 75.0 | 71.3 | 35.6 | |
| 5.2 | 76.1 | 78.8 | 77.9 | 84.5 | 82.6 | | 80.2 | 80.4 | 106.1 | 64.8 |
| 5.3 | 89.5 | 94.8 | 94.1 | 94.2 | 92.4 | | 85.2 | 85.1 | 100.6 | 67.3 |
| 5.4 | 92.3 | 98.1 | 96.7 | 96.1 | 94.7 | | 94.8 | 94.7 | 103.6 | |
| 5.5 | 28.5 | 32.1 | 31.9 | 27.6 | 26.0 | | 25.5 | 22.9 | 43.1 | 30.0 |
| Nonplanar Model: OH to OH Transfer | | | | | | | | | | |
| barrier (TS) | 64.6 | 67.9 | 58.7 | 70.9 | | | 64.9 | 65.3 | 85.8 | |
| product | 2.8 | 6.1 | 8.7 | 5.8 | | | 1.4 | 1.3 | 44.7 | 25.1 |

^aThe inclusion of zero-point energies is denoted with “+zpe”.

Table 7. Average Absolute and Maximum Errors Compare with the CCSD(T) Results as a Function of Basis Set Used in the CCSD(T) Calculation

| method | basis set | | | | | |
|----------------------------|-----------|------|---------|------|---------|------|
| | 6-31G** | | cc-pVTZ | | cc-pVQZ | |
| | avg | max | avg | max | avg | max |
| Bond and Reaction Energies | | | | | | |
| no. of cases | 31 | | 19 | | 9 | |
| B3LYP | 2.9 | 12.3 | 3.6 | 8.6 | 3.8 | 7.0 |
| PW91 | 4.7 | 18.7 | 4.5 | 14.9 | 4.9 | 8.3 |
| DFTB(mio) | 19.2 | 41.2 | 18.2 | 37.6 | 24.4 | 31.3 |
| DFTB(pbc) | 18.6 | 41.9 | 15.0 | 38.1 | 22.4 | 36.9 |
| ReaxFF | 23.3 | 50.4 | 20.0 | 41.3 | 23.1 | 40.8 |
| no. of cases | 27 | | 18 | | 8 | |
| ReaxFF relaxed | 11.6 | 26.9 | 11.6 | 25.1 | 9.5 | 19.7 |

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