Supplementary data for the mechanism research for depolymerization of cellulose induced by hydroxyl radical using GC–MS, reaction kinetics simulation and quantum chemistry computation

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**Abstract**

This data article contains the chemical structure of cellobiose, which was chosen as the model molecule of cellulose. A brief diagram of the reaction system established by Packmol containing celluloses, hydroxyl radicals and water for ReaxFF kinetic simulation as well as the energy change curve obtained during the optimization process were provided. The total ion current (TIC) and product species of the reaction of cellobiose with Fenton’s regent given by GC-MS were displayed, respectively. A brief diagram of the OH-abstraction of cellobiose triggered by hydrated hydrogen radical was shown. Additionally, chemical structures of all transition states in pathways 1–4 of the reaction of cellobiose with \( \bullet \text{OH} \) carried out by means of quantum calculation using Gaussian 09 are shown. Some key frames in reaction pathway 1 obtained by ReaxFF simulation and the thermodynamic parameters for reaction pathways 1–4 were also listed successively. Interpretation of this data can be found in a research article titled “Study on Cellulose Degradation Induced by Hydroxyl Radical with...”
Cellobiose as a Model Using GC-MS, ReaxFF Simulation and DFT Computation” (Shao et al., 2020) [1]. © 2020 Published by Elsevier Inc. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Data

Data provided in this article are based on GC-MS, ReaxFF kinetics simulation and DFT computation. The computation performed applying Gaussian 09 [1] at B3LYP/6-31 + G (d,p) level and are treated using ChemBioDraw Ultra 12.0 [2], Origin 9.0 or BIOVIA Discovery Studio Visualizer 2016 [3]. Cellubiose
was chosen as the model molecule and its chemical structure is shown in Fig. 1. The ReaxFF kinetics system established by Packmol [4] as well as the energy curve during the geometry optimization process by Materials Studio 8.0 [5] are shown in Fig. 2. In Fig. 3, the total ion current obtained by gas chromatography – mass spectra (GC-MS) and the product species based on different carbon atoms are displayed, the latter figure is done by origin 9.0. And in Fig. 4, a brief diagram of the hydroxyl group abstraction process induced by hydrated hydrogen radical is shown. Figs. 5–8 show the 3D structures of transition states in the reaction pathways 1 to 4.

Some key frames during reaction pathway 1 given by the ReaxFF kinetics simulation with Materials Studio 8.0, such as the H-abstraction, the formation of aldehyde groups as well as breakage of the glycosidic bond are listed in Fig. 9.

Thermodynamic parameters of pathways given by quantum calculation are listed in Table 1.

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**Fig. 1.** Cellobiose was chosen as the model of cellulose, the pyran rings were labelled A and B while the carbon atoms were labelled 1 to 6 and 1’ to 6’.

**Fig. 2.** The molecular system for ReaxFF kinetics simulation. (a) The system established by packmol; (b) the energy curve during geometry optimization (The green molecules refer to cellobiose while others are hydroxyl radicals and water molecules). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
Fig. 3. GC-MS results of the reaction of cellobiose with Fenton’s regent. (a) Total ion current (TIC) given by GC-MS; (b) the product species with different carbon atoms, 27 compounds, including 25 carbon containing components and a couple of inorganic acids (compound 4 and 6), were identified by means of NIST 11.

Fig. 4. A brief diagram of the OH-abstraction of cellobiose triggered by hydrated hydrogen radical.
Fig. 5. The chemical structures of all the transition states of reaction pathway 1.
Fig. 6. The chemical structure of all the transition states of reaction pathway 2.
Fig. 7. The chemical structure of all the transition states of reaction pathway 3.
Fig. 8. The chemical structure of all the transition states of reaction pathway 4.
2. Experimental design, materials and methods

A Trace 1310 gas chromatograph (Thermo, USA) equipped with an ISQ single quadrupole mass spectrometer (Thermo, USA) and a MP–5 ms gas chromatographic column (0.25 mm × 30 m × 0.25 μm, Agilent, USA) was used for the GC-MS analysis. Analysis of GC-MS was performed using the Thermo Fig. 9. Some key frames in reaction pathway 1 obtained from ReaxFF simulation given by Materials Strudio 8.0.
| Species                      | $E$ (A.U.) | $\Delta E$ (kcal/mol) | Imaginary frequencies |
|-----------------------------|------------|------------------------|-----------------------|
| **Reaction pathway 1**      |            |                        |                       |
| Cellobiose + $\bullet$/OH  |            |                        |                       |
| TSI1                       | −1373.80018994 | 2.79                   | −254.8448             |
| IM1                        | −1297.37289889 | 3.84                   | −181.7516             |
| TSI2                       | −1297.36573672 | 4.18                   | −1210.6476            |
| IM3 + $\bullet$/OH         | −1372.40518022 | 8.69                   | −578.2651             |
| TSI4                       | −1296.15615717 | 10.40                  | −372.2592             |
| IM5                        | −1297.30024826 | 11.76                  | −177.7205             |
| TSI5                       | −1297.37289889 | 15.7                   | −88.4025              |
| IM6                        | −1297.30024826 | 15.7                   | −88.4025              |
| **Reaction pathway 2**      |            |                        |                       |
| Cellobiose + $\bullet$/OH  |            |                        |                       |
| TSI1                       | −1373.79117764 | 1.02                   | −888.4194             |
| IM7                        | −1297.38051267 | 1.44                   | −362.4149             |
| TSI2                       | −1374.97667174 | 3.79                   | −15.3957              |
| IM8                        | −1222.11611902 | 2.45                   | −26.6661              |
| TSI4                       | −1222.0538359 | 2.91                   | −54.8196              |
| IM9                        | −1297.35048791 | 6.33                   | −394.7160             |
| TSI5                       | −1106.37433006 | 6.33                   | −394.7160             |
| IM10 + P7                  | −915.66206851 | 3.15                   | −183.7358             |
| TSI6                       | −915.69544552 | 3.15                   | −183.7358             |
| IM12                       | −992.03362568 | 3.15                   | −183.7358             |
| TSI8                       | −992.01916563 | 14.87                  | −98.9341              |
| IM13 + P4 + P8             | −228.357657028 | 5.33                   | −98.9341              |
| TS9                        | −228.33836401 | 5.33                   | −98.9341              |
| **Reaction pathway 3**      |            |                        |                       |
| Cellobiose + $\bullet$/OH  |            |                        |                       |
| TSI11                      | −1374.96156176 | 19.52                  | −20.6975              |
| IM14                       | −1374.98418693 | 12.46                  | −539.2050             |
| TSI12                      | −1374.97667174 | 3.79                   | −15.3957              |
| IM15                       | −1222.11844387 | 4.01                   | −132.1112             |
| TSI31                      | −878.49163879 | 4.82                   | −154.0470             |
| IM19                       | −878.495438060 | 13.52                  | −364.0099             |
| TSI6                      | −954.883306720 | 13.52                  | −364.0099             |
| IM20 + P9                  | −954.894062195 | 13.52                  | −364.0099             |
| TSI7                       | −610.124246923 | 9.59                   | −55.0716              |
| IM21 + P2                  | −610.148031871 | 9.59                   | −55.0716              |
| TS9                        | −382.198292315 | 1.96                   | −609.7246             |
| **Reaction pathway 4**      |            |                        |                       |
| Cellobiose to P10 + P11    |            |                        |                       |
| TSI1                        | −1373.82600309 | 3.41                 | −18.6029              |
| IM22                       | −1373.83363056 | 7.62                  | −21.4939              |
| TSI2                       | −1297.37232738 | 7.62                  | −21.4939              |
| IM23 + P10                 | −1297.37560601 | 7.62                  | −21.4939              |
| TSI3                       | −611.331097178 | 9.94                   | −70.3568              |
| IM24                       | −611.343289532 | 9.94                   | −70.3568              |
| TSI4                       | −610.773383274 | 2.31                   | −4.9432               |
Xcalibur Qual software [6]. Identification of compounds was carried out by comparing the mass spectra to the standard library NIST11 [7,8].

The chemical structure schemes were generated by using BIOVIA Discovery Studio Visualizer 2016 based on the TS optimization of the corresponding transition states with Gaussian 09 at B3LYP/6-31 + G (d,p) level.

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Conflict of 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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