Data Article

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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A R T I C L E   I N F O

A B S T R A C T

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 •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].

Specifications Table

Subject	Chemistry, Physical and Theoretical Chemistry
Specific subject area	Radical degradation mechanism of carbohydrate
Type of data	Table, Figure, Graph, Chart, Schematic diagram, Image.
How data were acquired	Schematic diagram from ChemBioDraw Ultra 12.0.
	GC-MS spectra collected using Thermo Trace 1310 with MS standard library NIST11 and the bar charts made by Origin 9.0.
	Structures of transition states and energy data from Gaussion09.
	ReaxFF reaction kinetics simulation using Material Studio 8.0.
Data format	Data of current article
Parameters for data collection	The MS samples were derived with O-methyl hydroxylamine hydrochloride/pyridine and N-methyl-N-(trimethylsilyl) trifluoroacetamide. The temperature of the injector was set at 250 °C, the flow rate of the carrier gas (helium) was 1.00 mL/min and the split ratio was 10:1. The temperature of the column was set to keep at 110 °C for 2 min at first, then raised to 160 °C at 8 °C/min, to 230 °C at 2 °C/min, to 250 °C at 5 °C/min and kept for 10 min. The injection volume was 1.0 μL.
	Quantum chemistry calculation with B3LYP/6-31 + G (d,p) level and PCM solvent model.
	ReaxFF reaction kinetics simulation using Reaxff 6.0 forcefield in GULP module of Material Studio 8.0.
Description of data collection	The structure of Figs. 1 and 4 were drawn using ChemBioDraw Ultra 12.0. Fig. 2 was collected by Material Studio 8.0. Fig. 3(a) was given by Trace 1310 GC-MS and the data in Fig. 3(b) was collected from the identification of compounds in MS by comparing the mass spectra to the standard library NIST11 and the bar chart was made by Origin 9.0. Figs. 5—8 were the transition states in the reaction pathways 1 to 4 from DFT calculation at B3LYP/6-31 + G (d,p) using G09 and the images were made by BIOVIA Discovery Studio Visualizer 2016. Fig. 9 was made by Material Studio 8.0. The data in Table 1 were obtained from the quantum chemistry calculation using Gaussion09 at B3LYP/6-31 + G (d,p) level with PCM aqueous solvent model.
Data source location	Tianjin, China Latitude and longitude:117.715812E, 39.093244 N.
Data accessibility	With the article
Related research article	C. Shao, Q. Shao, X. Wang, J. Ling, X. Guo, Y. Ning, Y. Dai, S. Jia, Y. Qiao, C. Li, K. Zhao. Study on cellulose degradation induced by hydroxyl radical with cellobiose as a model using GC—MS, ReaxFF simulation and DFT computation, Carbohydrate Polymers, 233 (2020) 115,677. https://doi.org/10.1016/j.carbpol.2019.115677

Value of the Data

- These data provide some details which can facilitate the readers' understanding of the related research article.
- All researchers and investigators who focused on the related research field can benefit from these data.
- These data could extend the readers' knowledge about the free radical degradation of cellulose.

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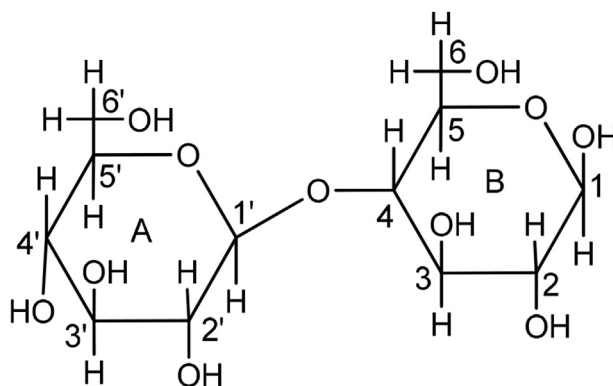
Fig. 1. Cellobiose was chosen as the model of cellulose, the pyran rings were labelled A and B while the carbon atoms were labelled 1 to 6 and 1′ to 6′.

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.
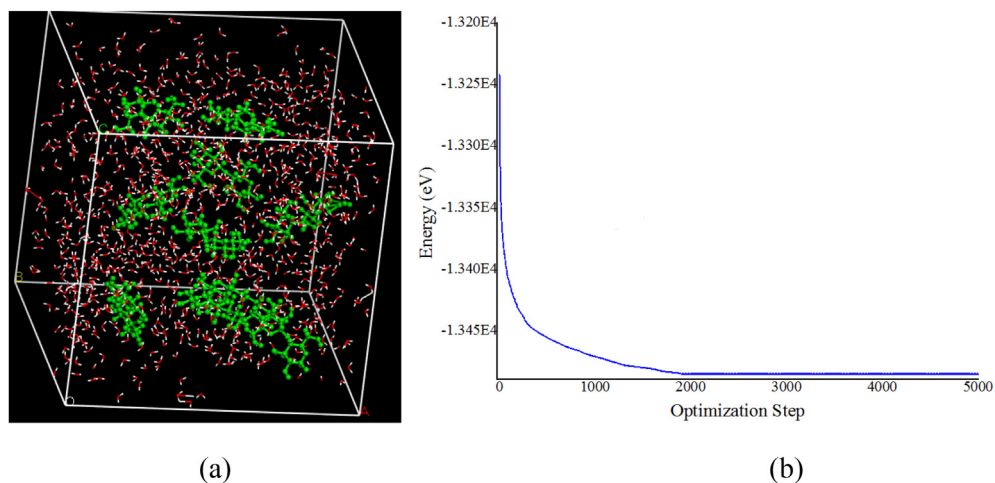

(a)   (b)

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.)
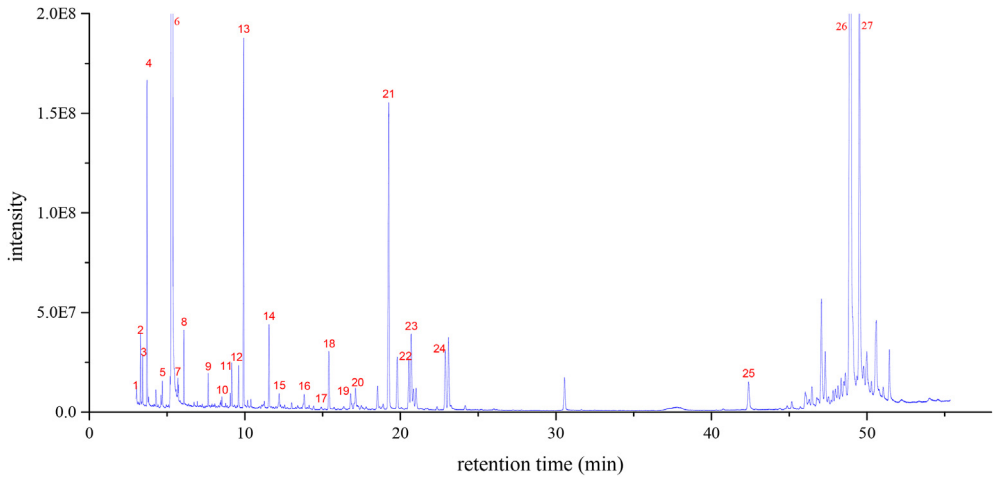
(a)
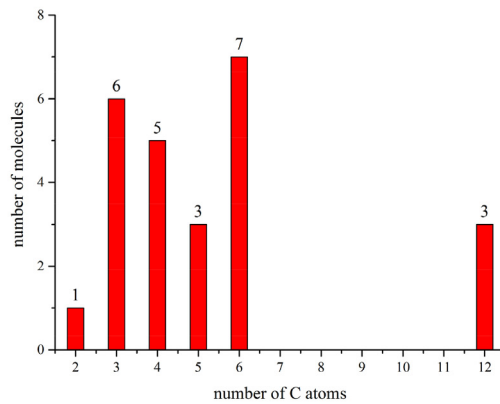
(b)

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.
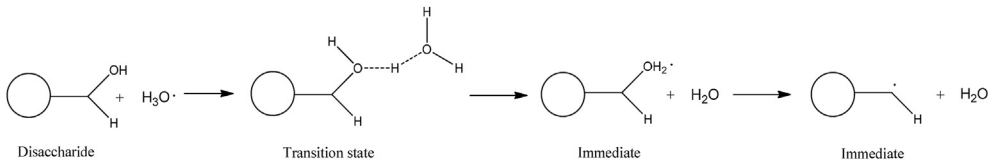

Fig. 4. A brief diagram of the OH-abstraction of cellobiose triggered by hydrated hydrogen radical.

TS$_I$1

TS$_I$2

TS$_I$3

TS$_I$4

TS$_I$5

TS$_I$6

TS$_I$7

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.
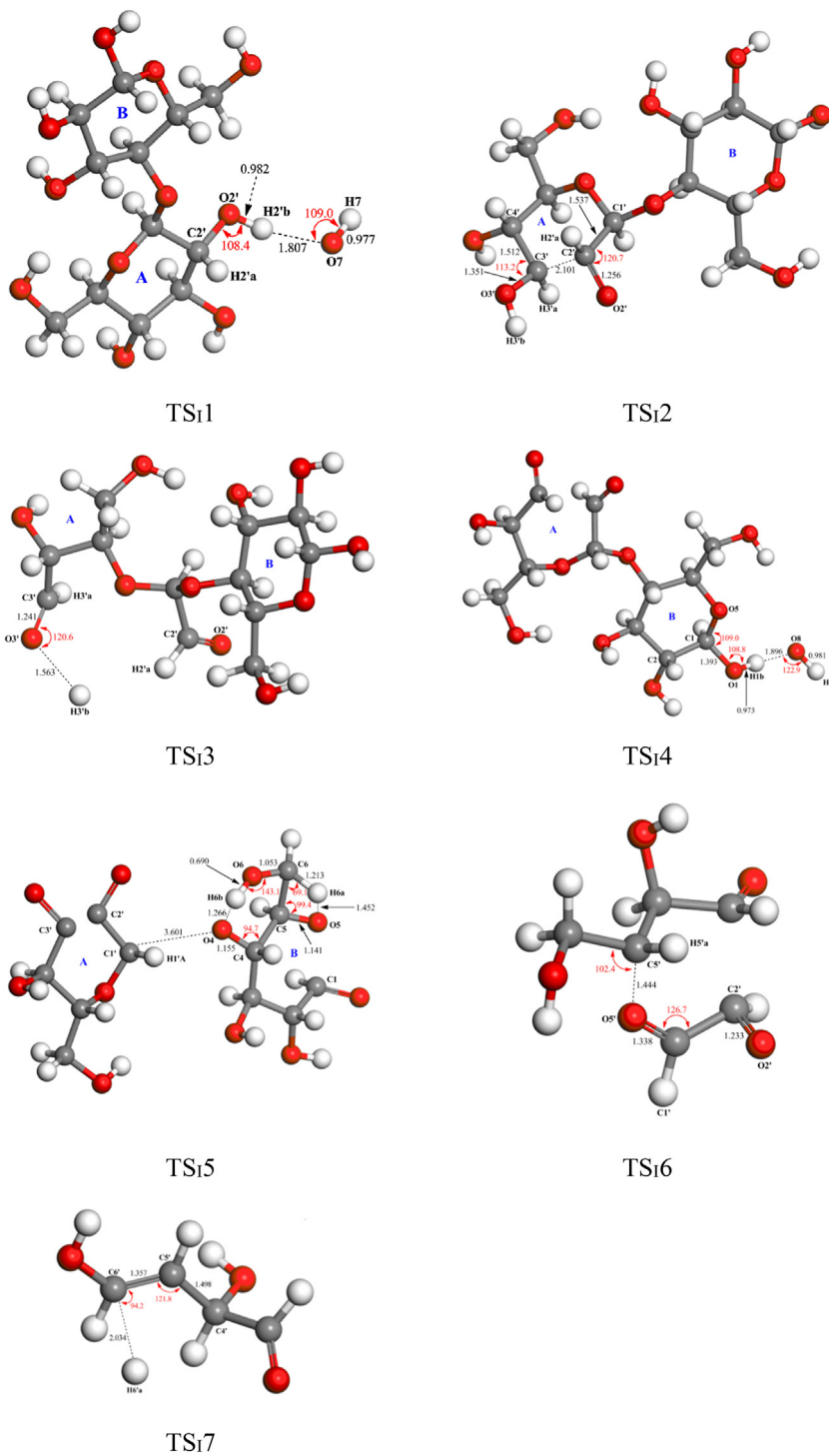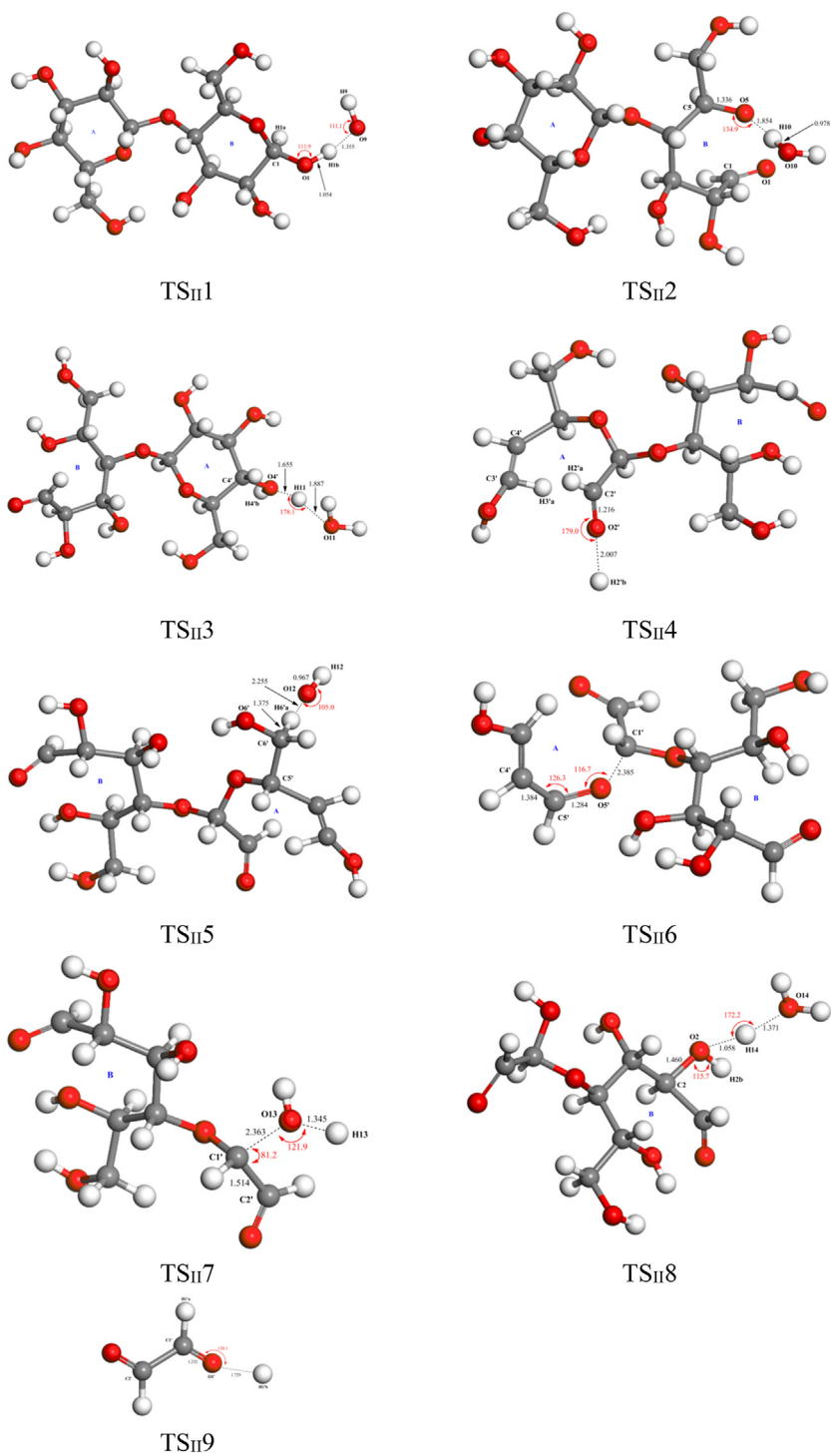
Fig. 7. The chemical structure of all the transition states of reaction pathway 3.

Fig. 8. The chemical structure of all the transition states of reaction pathway 4.
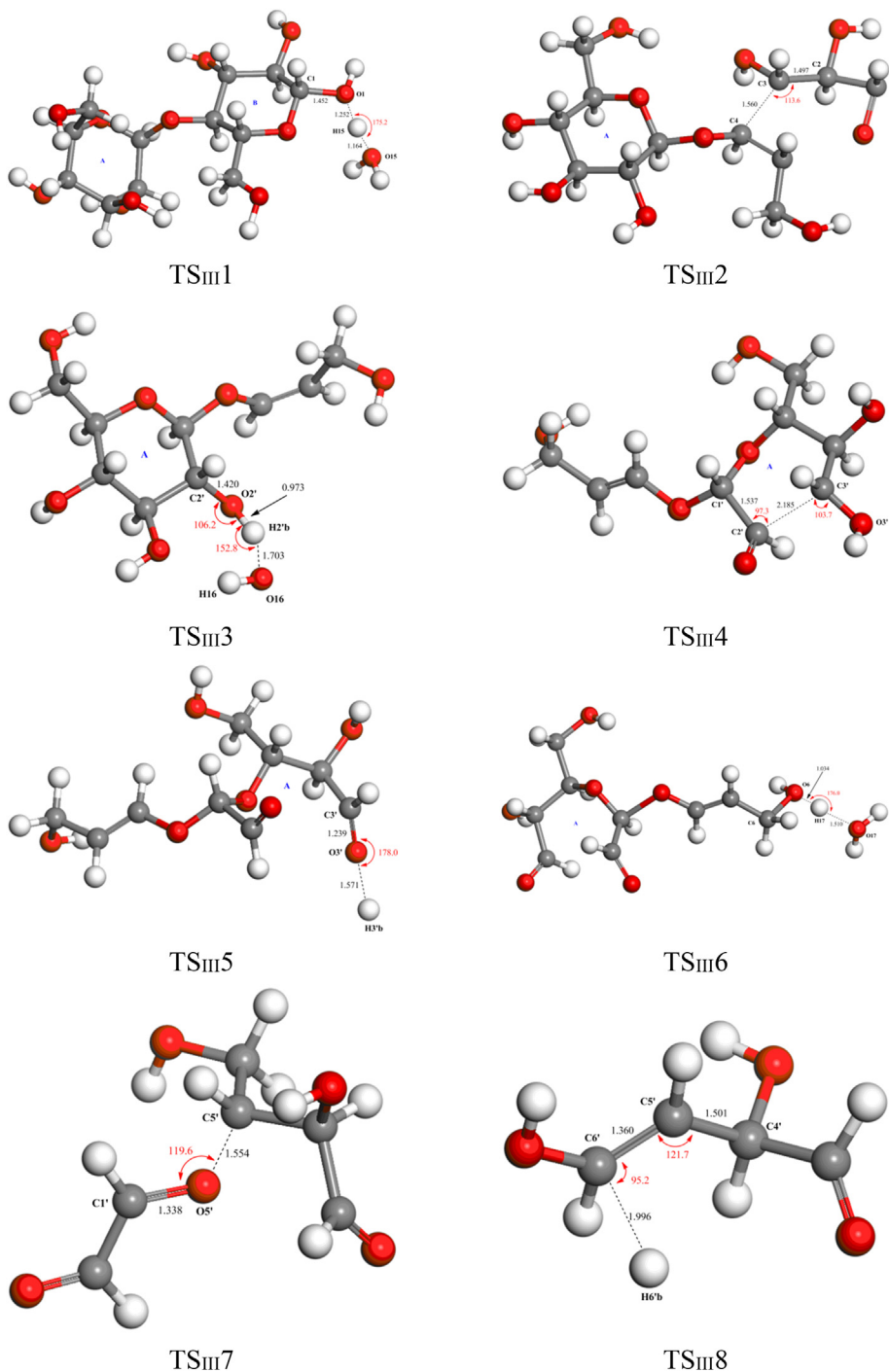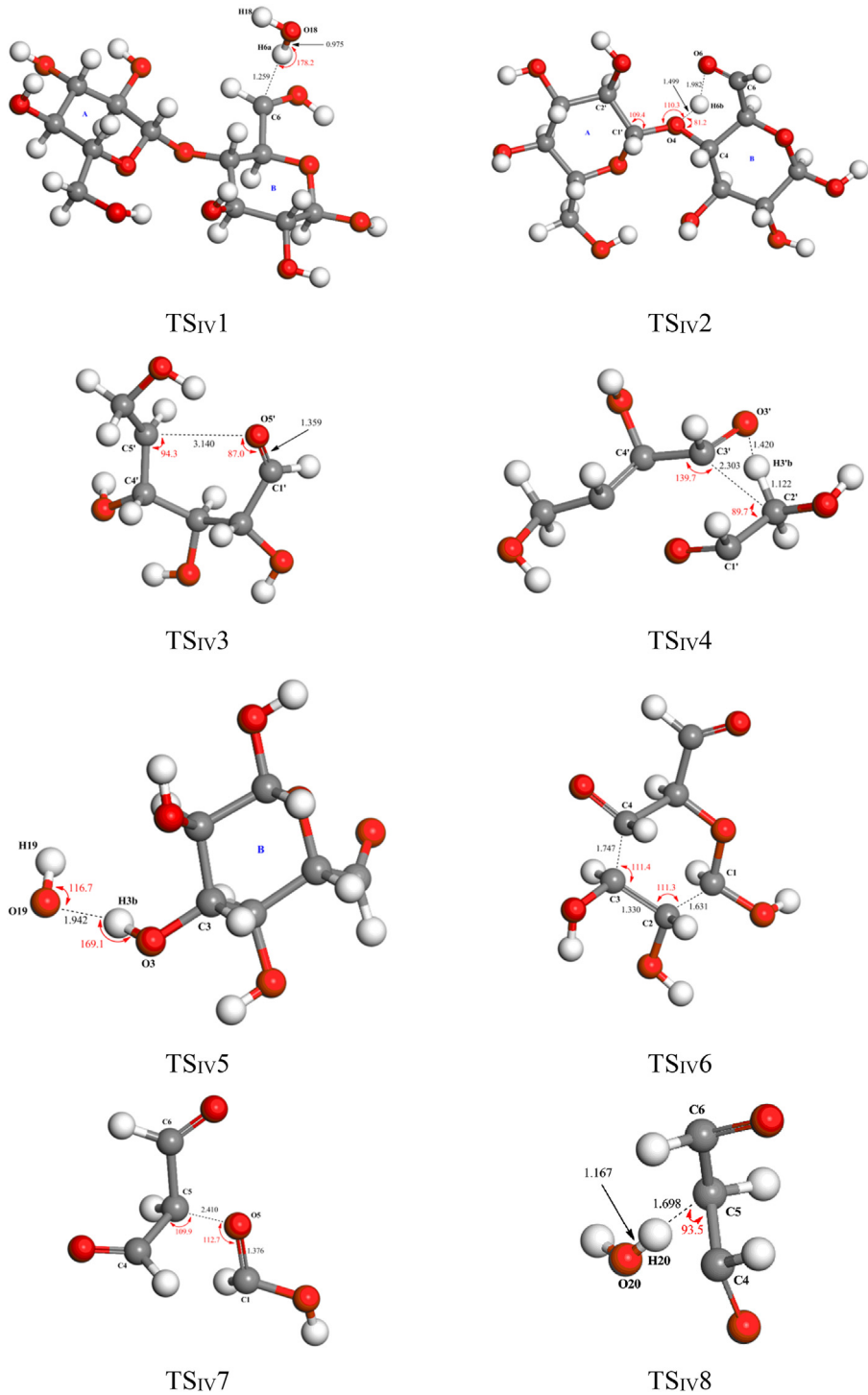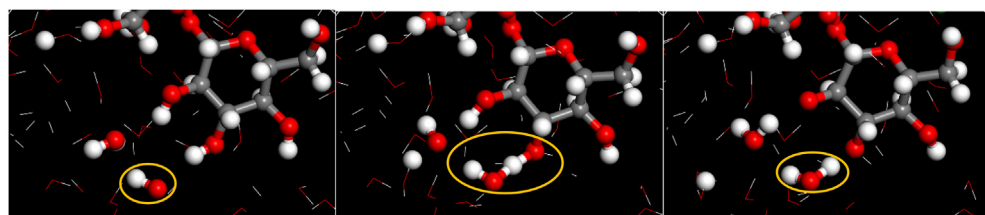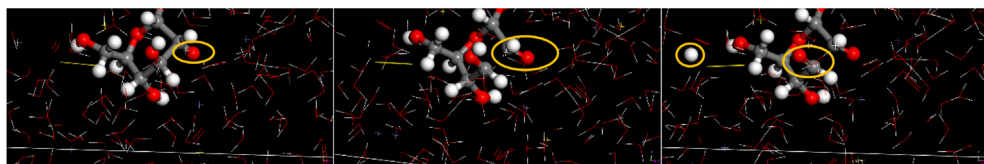
A hydroxyl radical is approaching its target H atom.
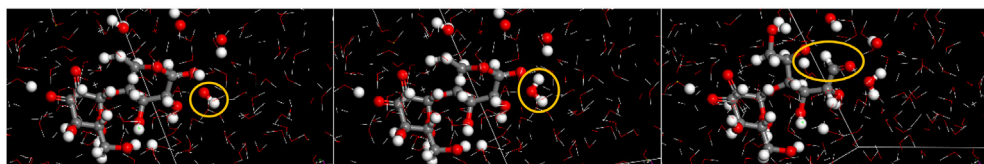
The radical combines with that H atom.

A water molecule is formed and drifting away.

The H atom on C2' has been abstracted.

The C2'–C3' bond breaks up and an aldehyde group is formed on C2'.

A second aldehyde group is formed on C3' while the H leaves the saccharide molecule.

A hydroxyl radical is approaching the H atom on C1, moiety B.

The H atom is abstracted and thus a water molecule is formed.

The C1–O bond is broken and a aldehyde group on C1 appears.
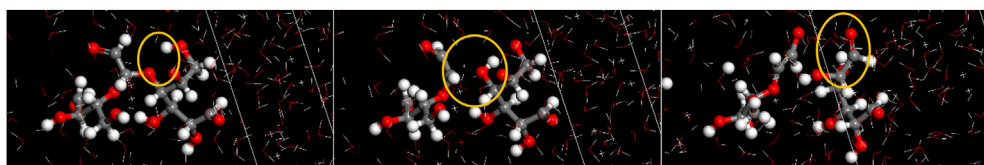
The H atom on C6 is moving towards the glycosidic O atom.

The H-transferring is done and the glycosidic bond is broken up.

After another H-transferring from C6 to C5, an aldehyde group is form on C6.

Fig. 9. Some key frames in reaction pathway 1 obtained from ReaxFF simulation given by Materials Strudio 8.0.

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

Table 1

Thermodynamic parameters of reaction pathway 1 given by quantum calculation.

Species	E (A.U.)	ΔE (kcal/mol)	Imaginary frequencies
Reaction pathway 1			
Cellobiose + •OH	−1373.80018994		
TS$_I$1	−1373.79517894	2.79	−254.8448
IM1	−1297.37289889		
TS$_I$2	−1297.36573672	3.84	−181.7516
IM2	−1297.30024826		
TS$_I$3	−1297.29356259	4.18	−1210−6476
IM3 + •OH	−1372.40518022		
TS$_I$4	−1372.39133055	8.69	−578.2651
IM4	−1296.15615717		
TS$_I$5	−1296.15593283	10.40	−372.2592
IM5	−610.07969778		
TS$_I$6	−610.06100125	11.76	−177.7205
IM6	−382.200029716		
TS$_I$7	−382.198054016	1.57	−88.4025
Reaction pathway 2			
Cellobiose + •OH	−1373.79706884		
TS$_{II}$1	−1373.79117764	1.02	−888.4194
IM7	−1373.80515267		
TS$_{II}$2	−1373.80129746	1.44	−362.4149
P6	−1374.97667174		
TS$_{II}$3	−1374.97189175	3.79	−15.3957
IM8	−1222.11611902		
TS$_{II}$4	−1222.0538359	2.45	−26.6661
IM9	−1297.35048791		
TS$_{II}$5	−1297.34439439	2.91	−54.8196
IM10 + P7	−1106.37433006		
TS$_{II}$6	−1106.36437043	6.33	−394.7160
IM11 + P8	−915.662806851		
TS$_{II}$7	−915.6594552	3.15	−183.7358
IM12	−992.033632568		
TS$_{II}$8	−992.019196563	14.87	−98.9341
IM13 + P4 + P8	−228.357657028		
TS$_{II}$9	−228.33836401	5.33	−981.8451
Reaction pathway 3			
Cellobiose + •OH	−1374.99075606		
TS$_{III}$1	−1374.96156176	19.52	−20.6975
IM14	−1374.98418693		
TS$_{III}$2	−1222.11844387	12.46	−539.2050
IM15	−1222.14881312		
TS$_{III}$3	−954.922663476	1.37	−823.4358
IM17	−954.950996012		
TS$_{III}$4	−878.492664121	4.01	−132.1112
IM18	−878.500865162		
TS$_{III}$5	−878.491636879	4.82	−154.0470
IM19	−878.495438060		
TS$_{III}$6	−954.883306720	13.52	−364.0099
IM20 + P9	−954.894062195		
TS$_{III}$7	−610.124246923	9.59	−55.0716
IM21 + P2	−610.148031871		
TS$_{III}$8	−382.198292315	1.96	−609.7246
Reaction pathway 4 (cellobiose to P10 + P11)			
Cellobiose + •OH	−1373.83149075		
TS$_{IV}$1	−1373.82600309	3.41	−18.6029
IM22	−1373.83363056		
TS$_{IV}$2	−1297.37321738	7.62	−21.4493
IM23 + P10	−1297.37560601		
TS$_{IV}$3	−611.331097178	9.94	−70.3568
IM24	−611.343289532		
TS$_{IV}$4	−610.773383274	2.31	−4.9432

Table 1 (*continued*)

Species	E (A.U.)	ΔE (kcal/mol)	Imaginary frequencies
Reaction pathway 4 (cellobiose to P8)			
Cellobiose + •OH	−1373.83149075		
$TS_{IV}1$	−1373.82600309	3.41	−18.6029
IM22	−1373.83363056		
$TS_{IV}2$	−1297.37321738	7.62	−21.4493
IM23 + IM25	−1297.37560601		
$TS_{IV}5$	−761.772136432	1.24	−32.1187
IM26	−761.803346865		
$TS_{IV}6$	−685.329217242	13.79	−416.2850
IM27 + P12	−685.346966712		
$TS_{IV}7$	−456.253820055	4.08	−330.7715
IM28 + P13	−456.260315463		
$TS_{IV}8$	−342.953813877	8.98	−46.5245

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.

Acknowledgements

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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