Supporting Information

Mechanisic Study on Cellobiose Conversion to 5-Hydroxymethylfurfural Catalyzed by Brønsted Acid with Counterpart Anions in Aqueous Solution

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Phys. Chem. Chem. Phys.

Catalog

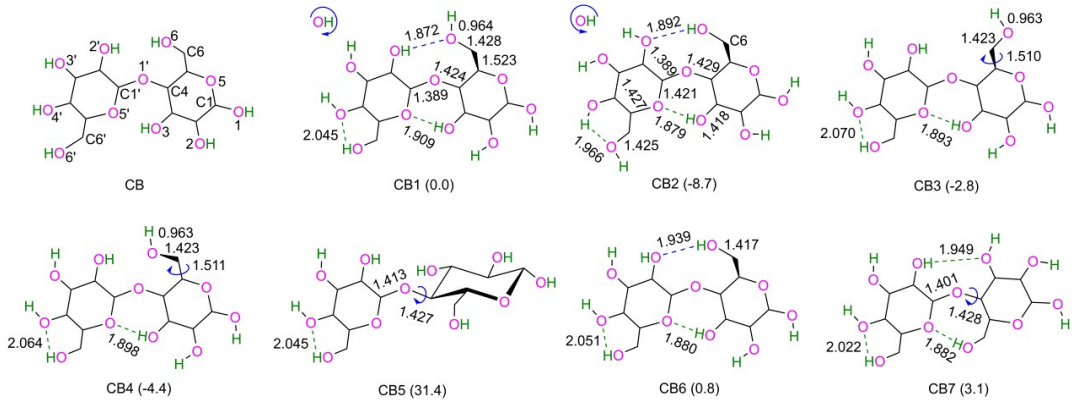

Figure S1. The geometric structures and the relative Gibbs free energy (ΔG, kJ mol^{-1}) relative to CB1 for seven configurations of *β*-cellobiose at M06-2x/6-311++G(d,p) level in aqueous solution under ambient temperature and pressure (298 K and 1 atm). For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å. CB1 (*syn-ϕ/syn-φ*), CB5 (*anti-ϕ/syn-φ*), and CB7 (*syn-ϕ/anti-φ*) are mutually conformers. CB1 (*tg*), CB3 (*gt*), and CB4 (*gg*) are mutually rotamers. CB1 (*c*), CB2 (*r*), and CB6 (*c*) are mutually anomers.

Notes:

Based on the reported configurations of *β*-cellobiose,[1-6] seven typical configurations are preferred as the models of subunits in cellulose in the present study. The geometric structures and relative Gibbs free energies of the seven typical configurations of *β*-cellobiose relative to CB1 are shown in Fig. S1. As depicted in Fig. S1, for the seven main configurations of *β*-cellobiose, the ΔG increases as CB2 < CB4 < CB3 < CB1 < CB6 < CB5 < CB7. It is indicated that the CB2 is thermodynamically most preferred among these seven configurations. Therefore, CB2 is preferred as the model molecule of cellulose in the present study, as it is the thermodynamically most stable subunit of crystalline cellulose $\mathbf{I}_\beta$. CB2 is associated with the C4–H4 and C1′–H1′ bonds nearly parallel on the glycosidic bonds, the hydroxymethyl groups (–CH_2OH) on opposite sides of the plane of the rings, the exocylcic hydroxyl groups with anticlockwise orientation, and three O6H···O2′, O3H···O5′, and O4′H···O6′ intramolecular H-bonds.

References:

1. S. Yan and L. Yao, *Carbohydr. Res.*, 2015, **404**, 117-123.
2. F. A. Momany and U. Schnupf, *Carbohydr. Res.*, 2011, **346**, 619-630.
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5. J. F. Matthews, M. Bergenstrahle, G. T. Beckham, M. E. Himmel, M. R. Nimlos, J. W. Brady and M. F. Crowley, *J. Phys. Chem. B*, 2011, **115**, 2155-2166.
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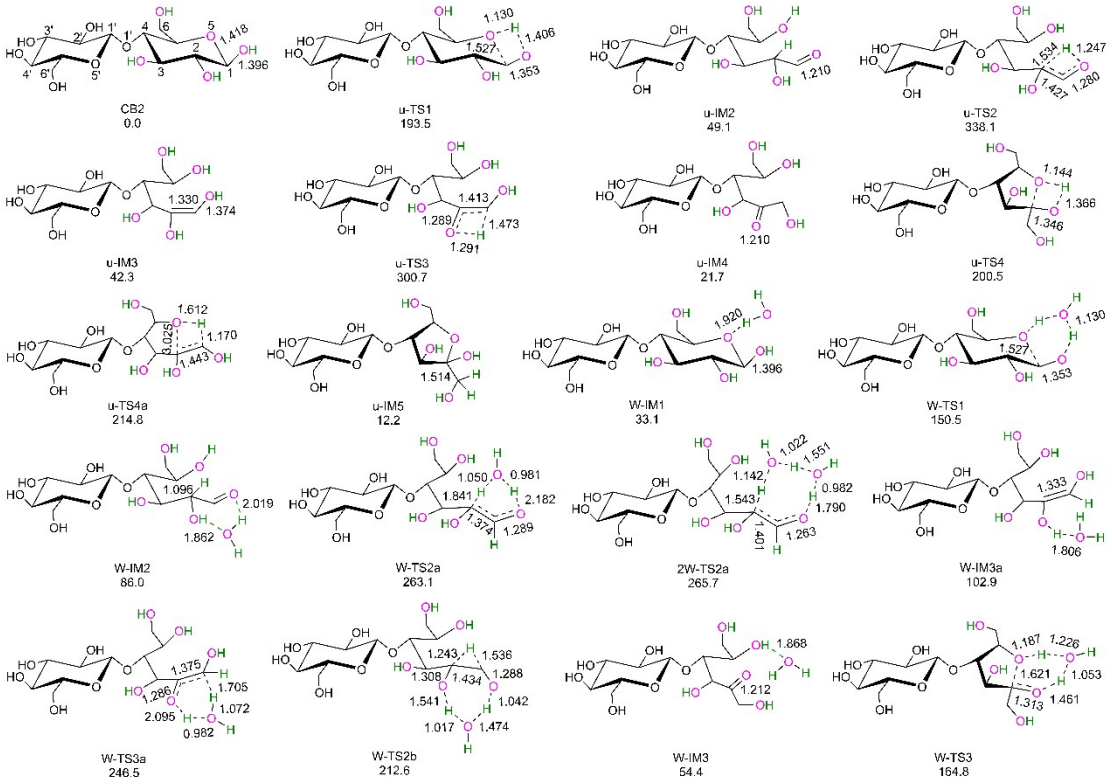
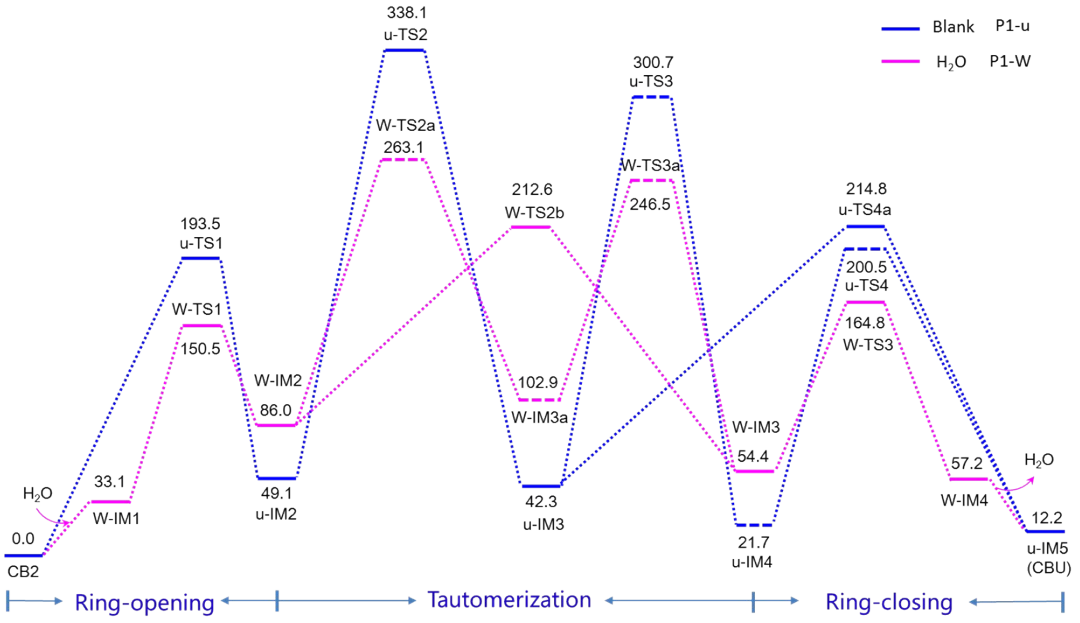


(a)

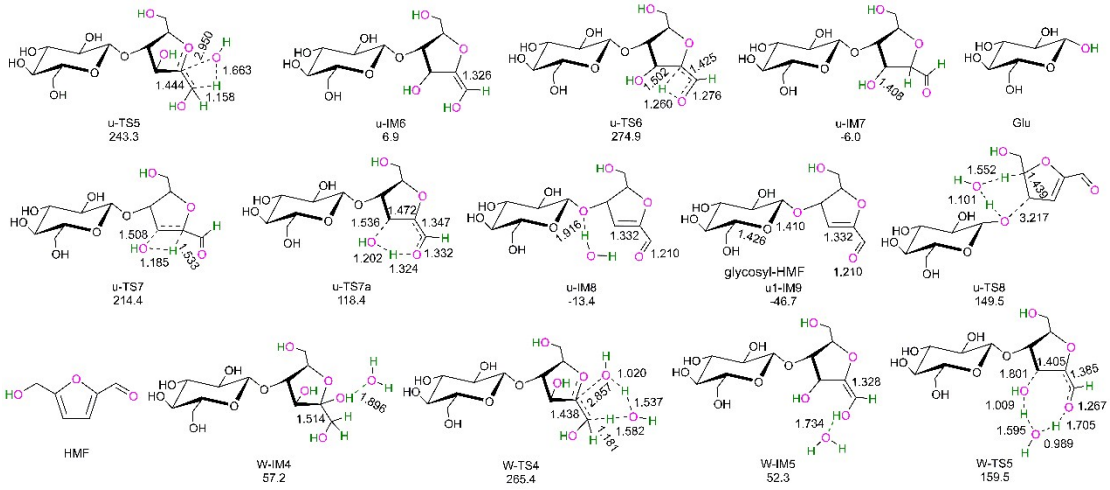


(b)

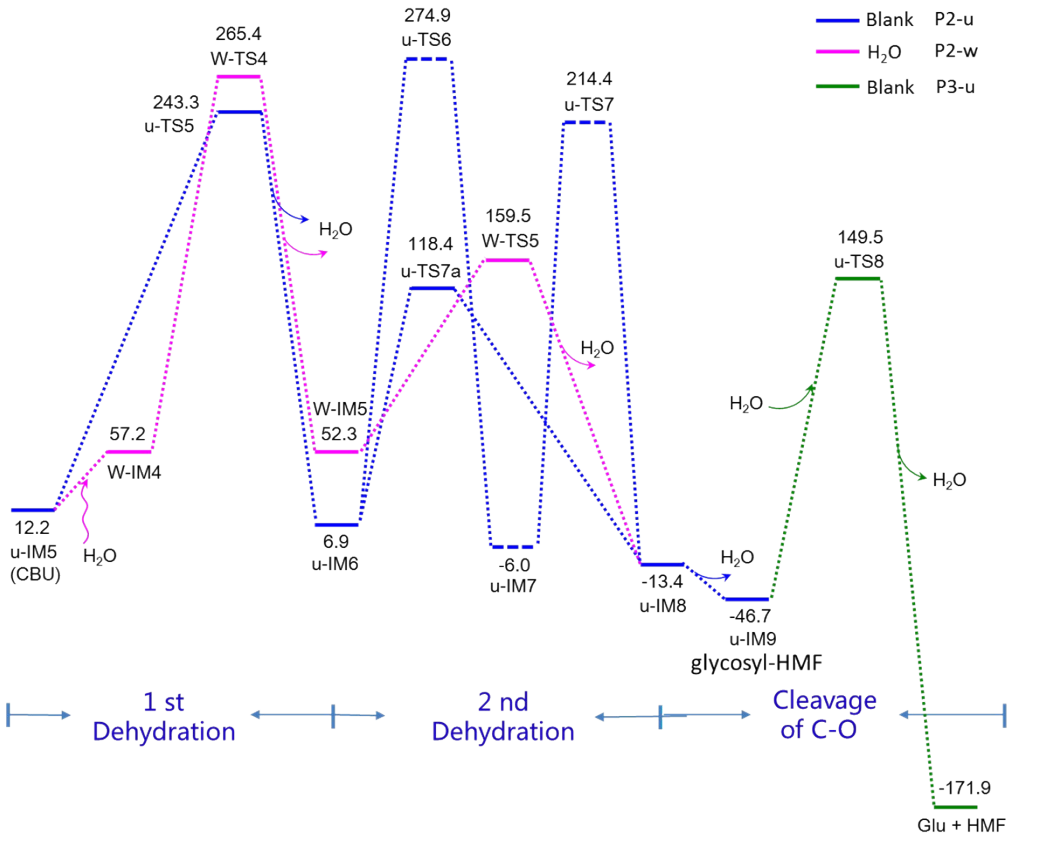
Figure S2. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the isomerization of *β*-cellobiose (CB2) to cellobiulose (CBU) in the absence of catalyst and in the presence of explicit H_2O in aqueous solution. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

Notes:

For exploring the catalytic performance of Brønsted acid, the blank reaction pathways for the isomerization of *β*-cellobiose to cellobiulose are studied in the absence of explicit H_2O and in the presence of explicit H_2O in aqueous solution. As indicated in Fig. S2, in the absence of explicit H_2O (**P1-u**), the minimal energy reaction pathway (MERP) includes the energy height of the highest point (EHHP) of 338.1 kJ mol^{-1} at u-TS2 and the highest energy barrier (HEB) of 289.0 kJ mol^{-1} at the reaction step of u-IM2 → u-TS2 → u-IM3. Alternatively, in the presence of explicit H_2O (**P1-w**), the MERP involves the EHHP of 212.6 kJ mol^{-1} at W-TS2b and HEB of 126.6 kJ mol^{-1} at the reaction step of W-IM2 → W-TS2b → W-IM3. It is obvious that **P1-w** possesses lower EHHP (212.6 *vs* 338.1 kJ mol^{-1}) and lower HEB (126.6 *vs* 289.0 kJ mol^{-1}) than **P1-u**. It is indicated that the explicit H_2O behaves as a catalyst toward the isomerization of *β*-cellobiose to cellobiulose.



(a)



(b)

Figure S3. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the conversion of cellobiulose (CBU) into glycosyl-HMF intermediate, glucose, and HMF in the absence of catalyst and in the presence of explicit H_2O in aqueous solution.

Notes:

As indicated Fig. S3, in the absence of explicit H_2O (P2-u), the MERP includes the EHHP of 243.3 kJ mol^{-1} at u-TS5 and HEB of 231.1 kJ mol^{-1} at the reaction step of CBU → u-TS5 → u-IM6. Alternatively, in the presence of explicit H_2O (P2-w), the MERP involves the EHHP of 265.4 kJ mol^{-1} at W-TS4 and HEB of 208.2 kJ mol^{-1} at the reaction step of W-IM4 → W-TS4 → W-IM5. It is indicated that the explicit H_2O does not show any catalytic activity toward the dehydration of cellobiulose to glycosyl-HMF. As shown in Fig. S3, the explicit H_2O acts as the reactant for the hydrolysis of glycosyl-HMF into discrete glucose and HMF, denoted as **P3-u**. The **P3-u** contains the EHHP of 149.5 kJ mol^{-1} at u-TS8 and HEB of 196.2 kJ mol^{-1} at the reaction step of glycosyl-HMF → u-TS8 → glucose + HMF.

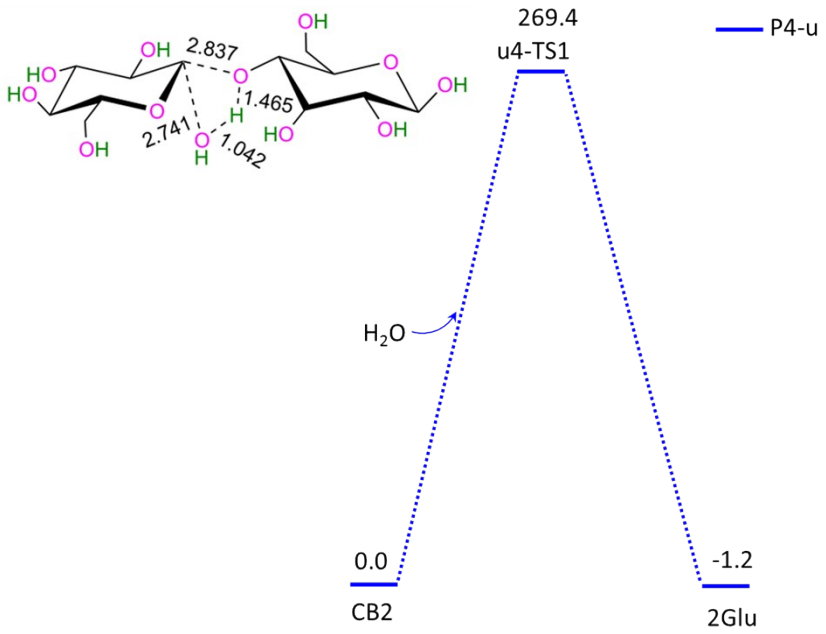
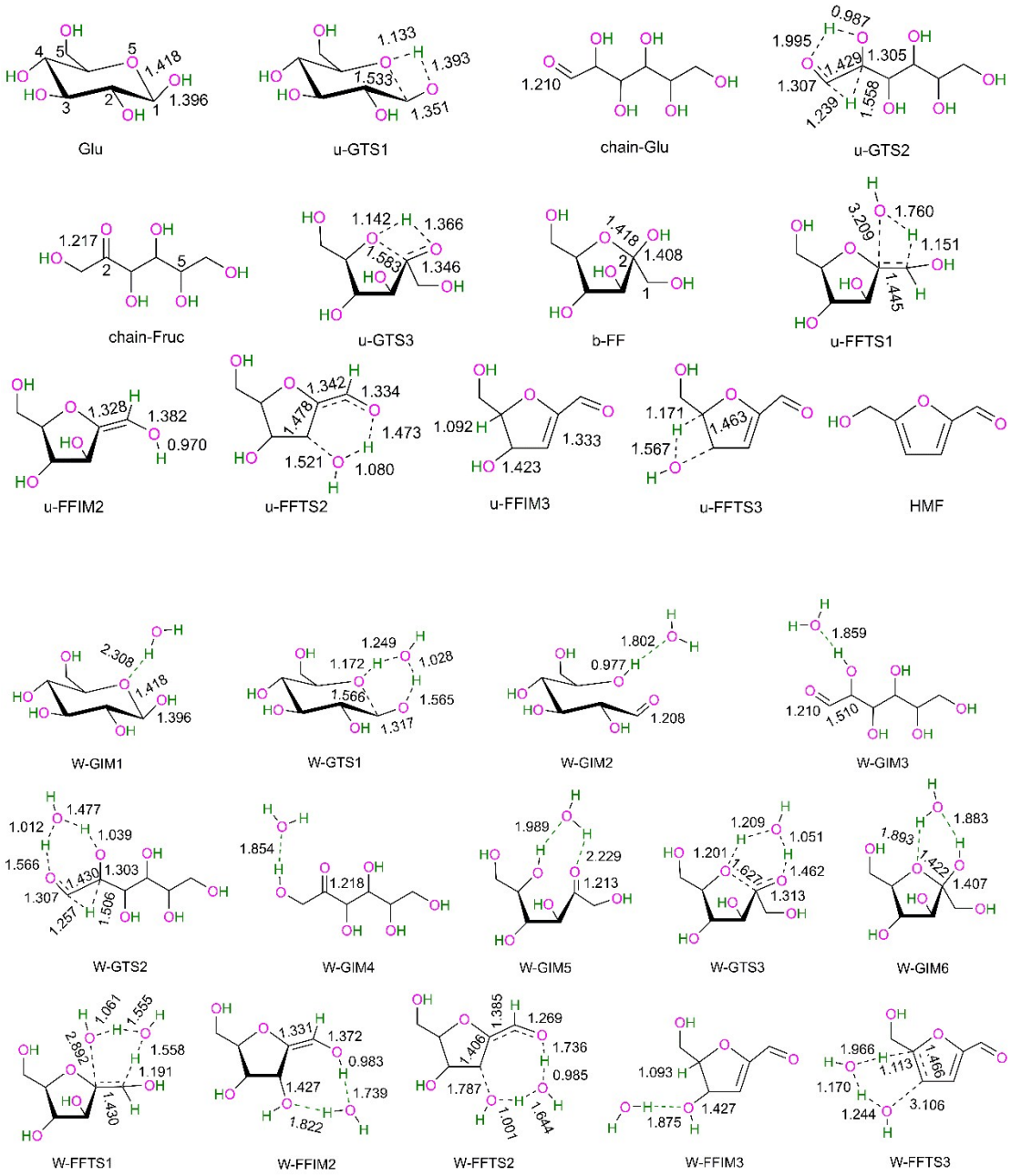


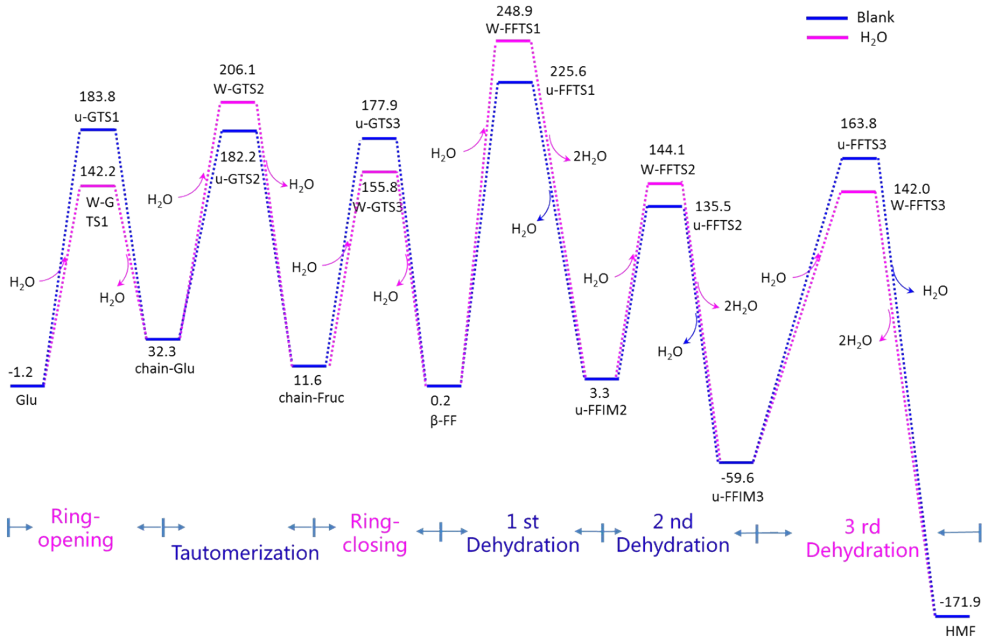
Figure S4. The geometric structures and schematic energy diagrams with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the hydrolysis of β-cellobiose (CB2) into glucose (Glu) in aqueous solution.

Notes:

As shown in Fig. S4, the explicit H_2O behaves as the reactant for the hydrolysis of β-cellobiose into two discrete glucose molecules, denoted as **P4-u**. The **P4-u** comprises the EHHP of 269.4 kJ mol^{-1} at u4-TS1 and HEB of 169.4 kJ mol^{-1} at the reaction step of CB2 + H_2O → u4-TS1 → 2×glucose.

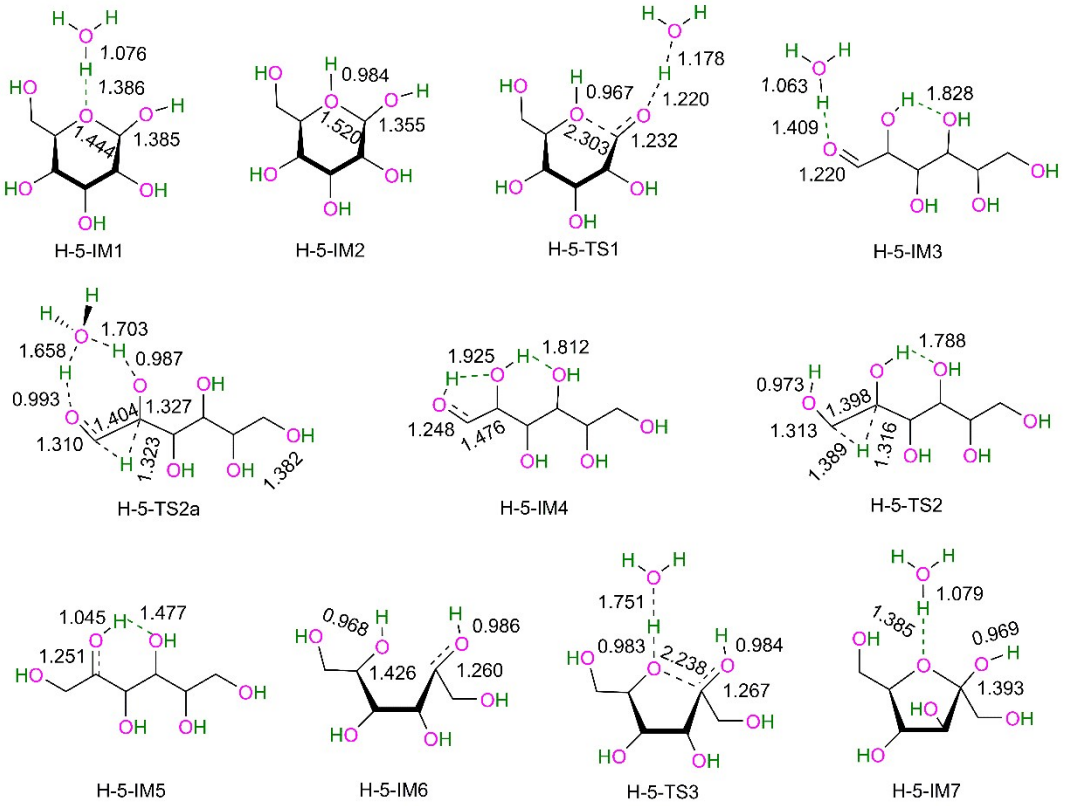

Glu
u-GTS1
chain-Glu
u-GTS2
chain-Fruc
u-GTS3
b-FF
u-FFTS1
u-FFIM2
u-FFTS2
u-FFIM3
u-FFTS3
HMF
W-GIM1
W-GTS1
W-GIM2
W-GIM3
W-GTS2
W-GIM4
W-GIM5
W-GTS3
W-GIM6
W-FFTS1
W-FFIM2
W-FFTS2
W-FFIM3
W-FFTS3

(a)

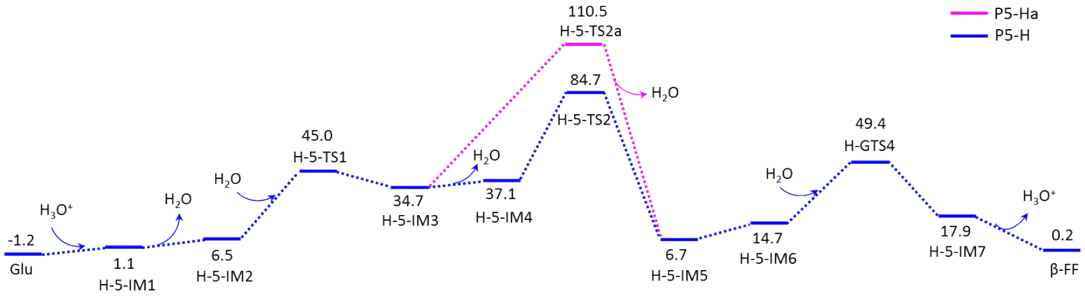


(b)

Figure S5. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the dehydration of β-D-glucopyranose (Glu) to 5-hydroxymethylfurfural (HMF) in the absence of catalyst and in the presence of explicit H_2O in aqueous solution.

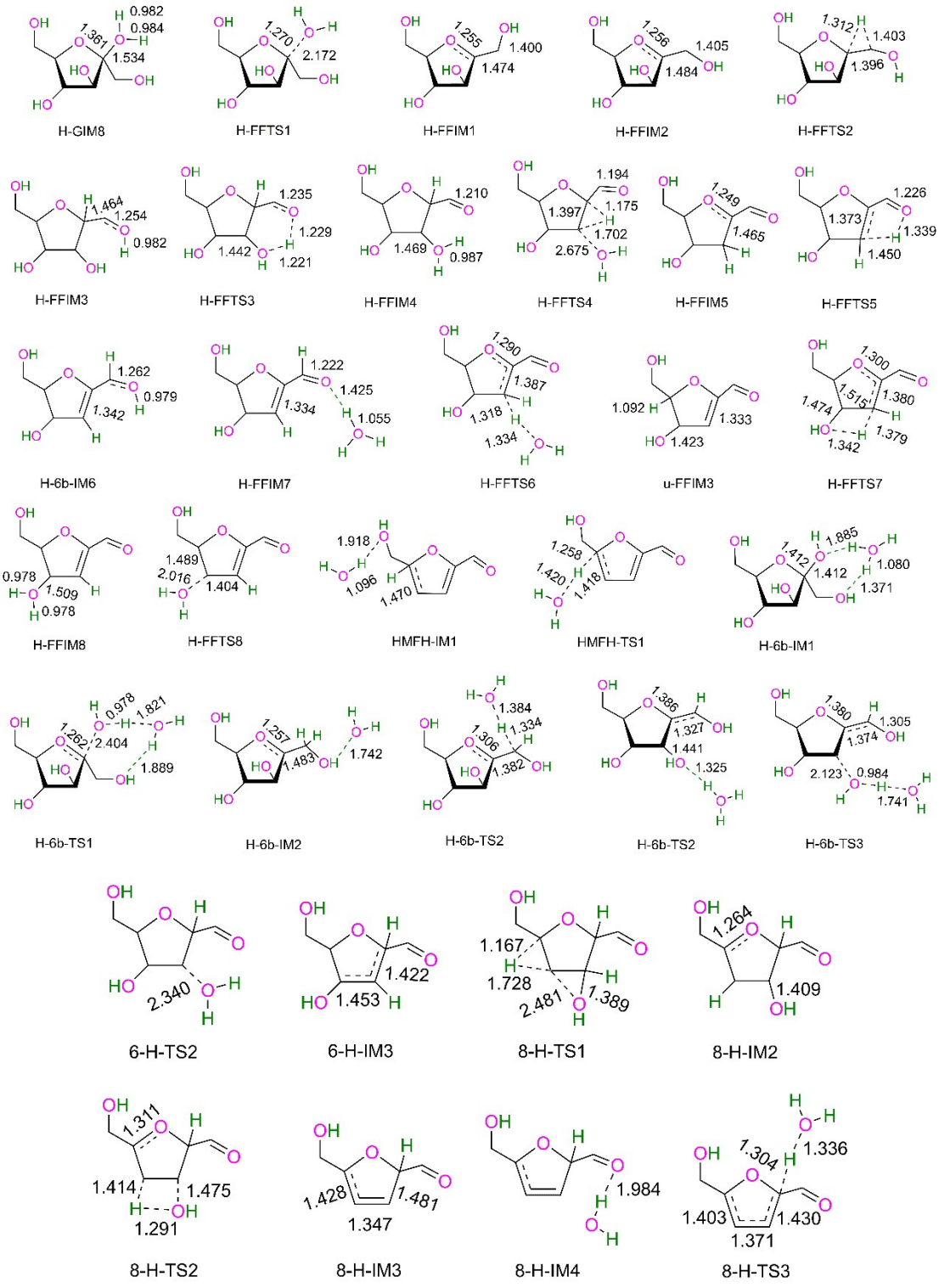


(a)



(b)

Figure S6. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the isomerization of *β*-D-glucopyranose (Glu) to *β*-D-fructofuranoses (*β*-FF) catalyzed by H_3O^+ in aqueous solution. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.


H-GIM8
H-FFTS1
H-FFIM1
H-FFIM2
H-FFTS2
H-FFIM3
H-FFTS3
H-FFIM4
H-FFTS4
H-FFIM5
H-FFTS5
H-6b-IM6
H-FFIM7
H-FFTS6
u-FFIM3
H-FFTS7
H-FFIM8
H-FFTS8
HMFH-IM1
HMFH-TS1
H-6b-IM1
H-6b-TS1
H-6b-IM2
H-6b-TS2
H-6b-TS2
H-6b-TS3
6-H-TS2
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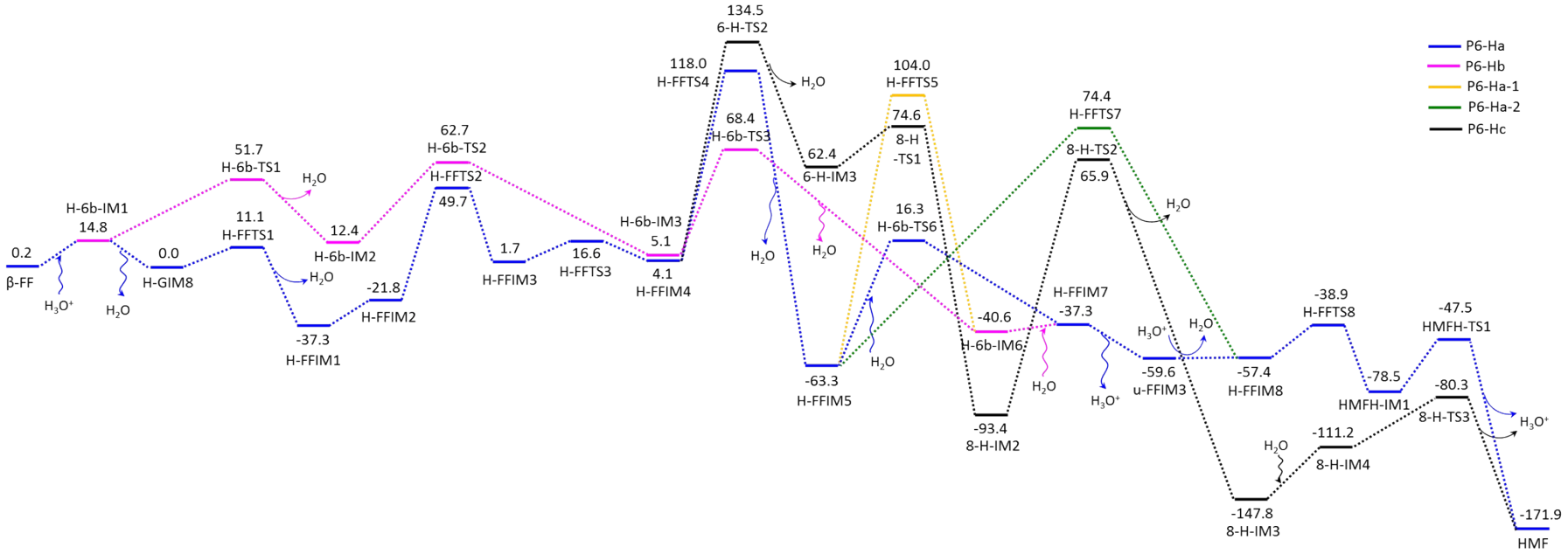
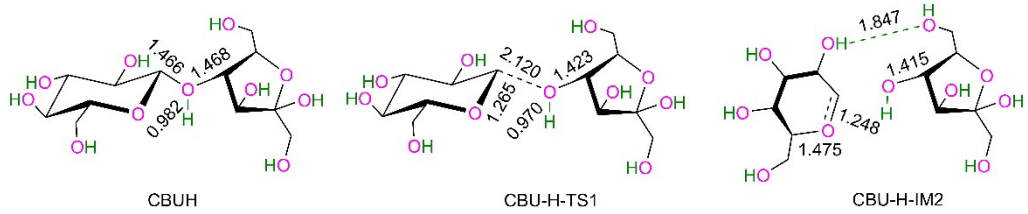
8-H-IM4
8-H-TS3

(a)

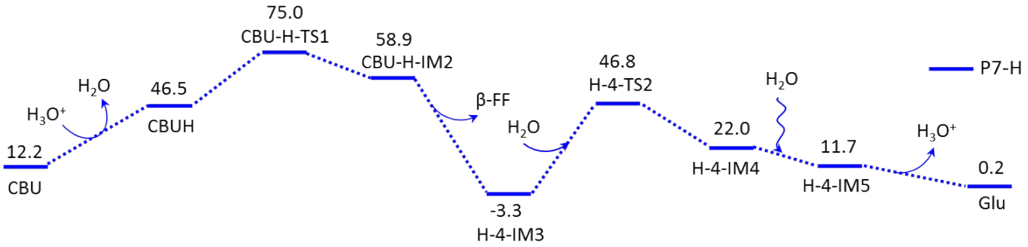


(b)

Figure S7. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the dehydration of *β*-D-fructofuranoses (*β*-FF) to 5-hydroxymethylfurfural (HMF) catalyzed by H_3O^+ in aqueous solution. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.



(a)



(b)

Figure S8. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the hydrolysis of cellobiulose (CBU) to glucose (Glu) and *β*-D-fructofuranoses (*β*-FF) catalyzed by H_3O^+ in aqueous solution. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

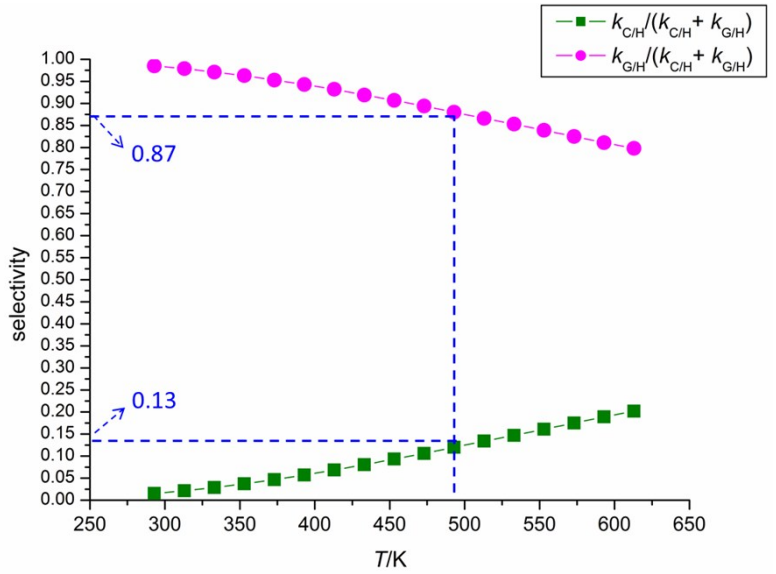


Figure S9. The selectivity of the reaction pathway through cellobiulose and glycosyl-HMF (**C/H**), through cellobiulose and fructose (**C/F/H**), and through glucose (**C/G/H**) for HMF origin. The selectivity of **C/G/H** is about 100% ~ 87%, while the selectivity of both **C/H** and **C/F/H** is about 0.0% ~ 13% over the temperature range of 293 ~ 493 K. That is to say, the origin of HMF stems from a small proportion of both **C/H** and **C/F/H** through cellobiulose, and from a large proportion of **C/G/H** through glucose.

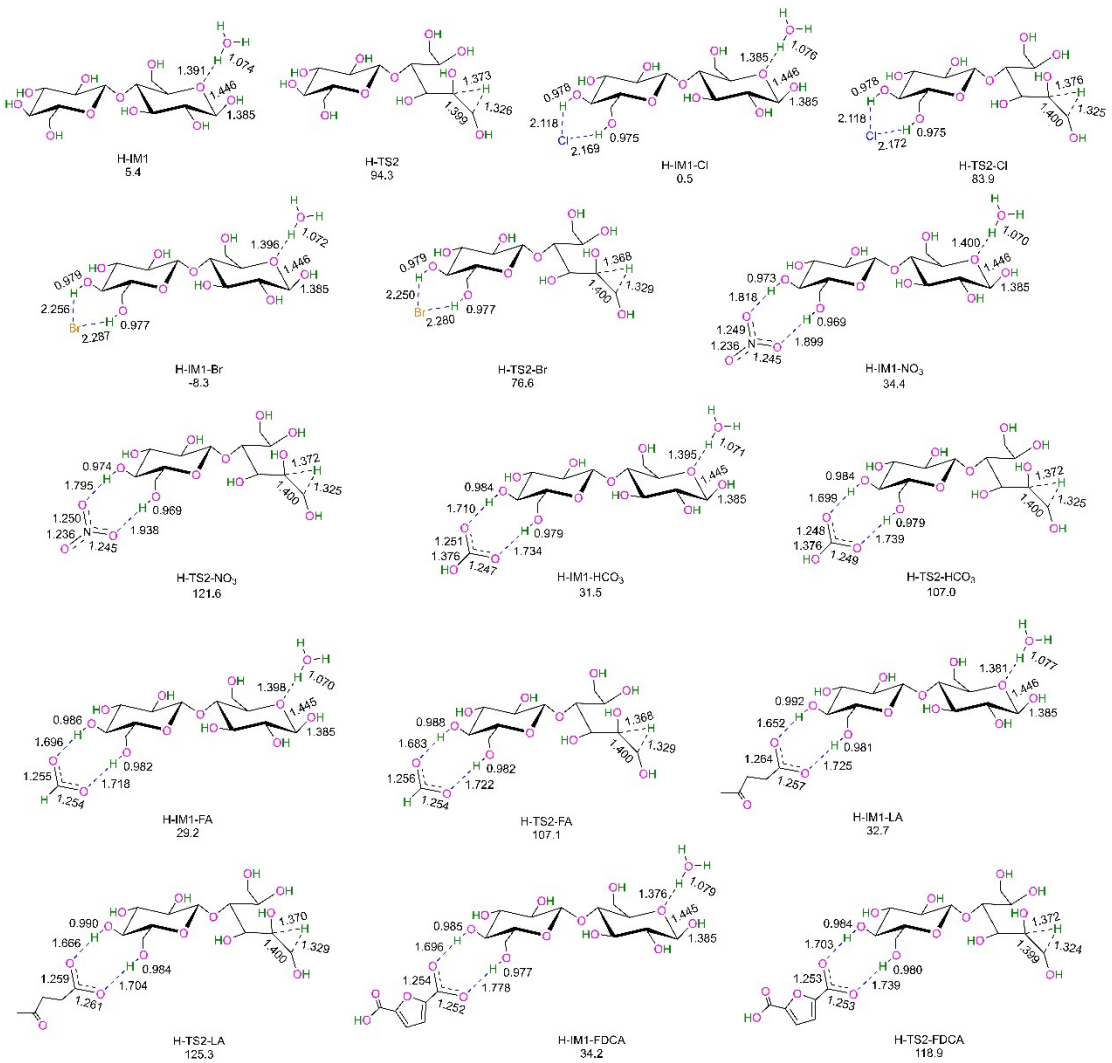


Figure S10. The geometric structures with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the conversion of *β*-cellobiose (CB) into both glucose and 5-hydroxymethylfurfural (HMF) in the presence of H_3O^+ alone and in the presence of H_3O^+ together with the counterpart anion (A^- = Cl^-, Br^-, NO_3^-, HCO_3^-, FA^-, LA^-, and $FDCA^-$) in aqueous solution. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

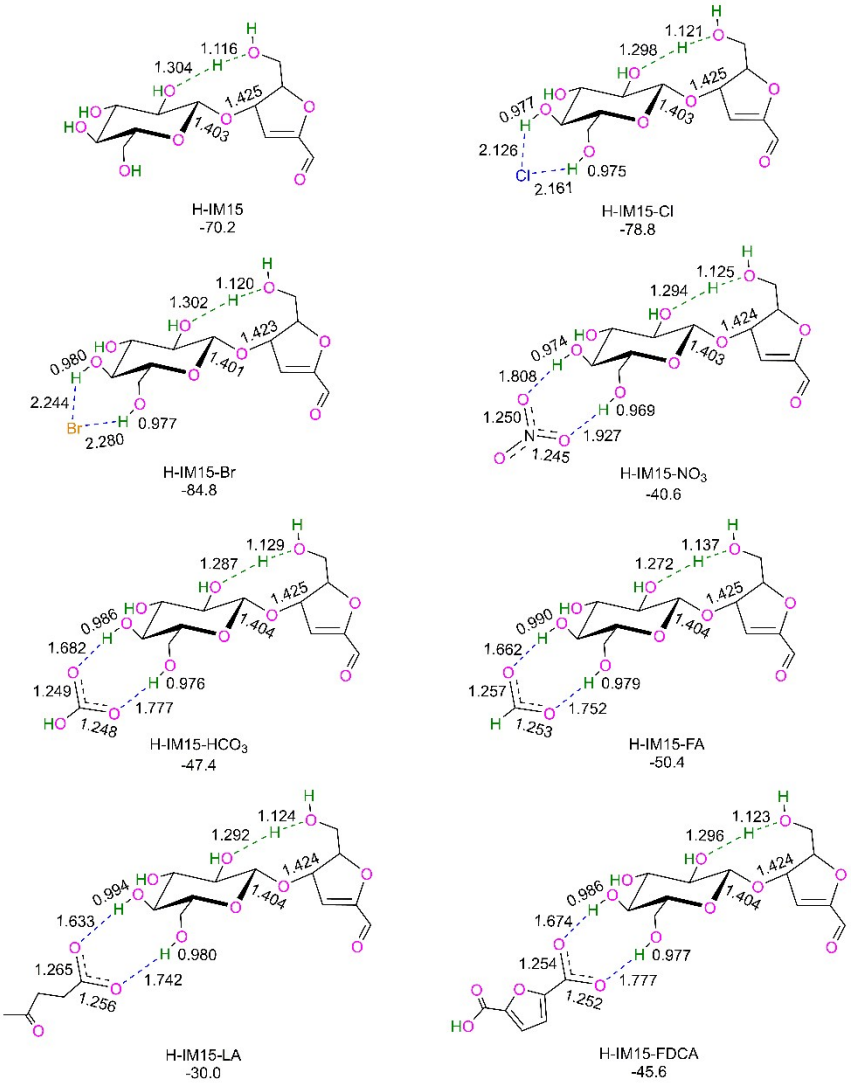
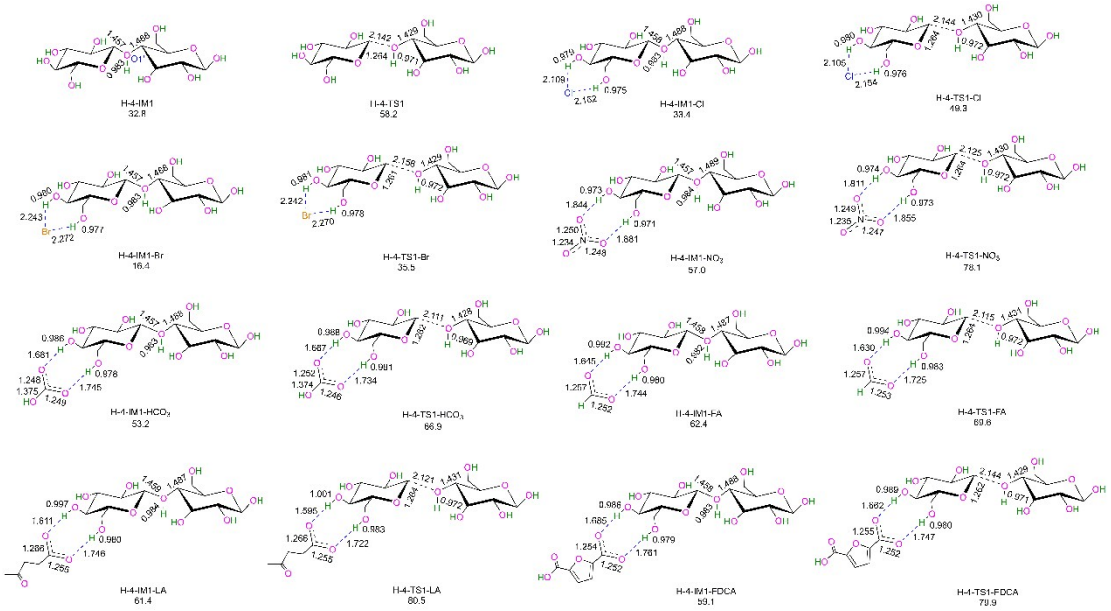
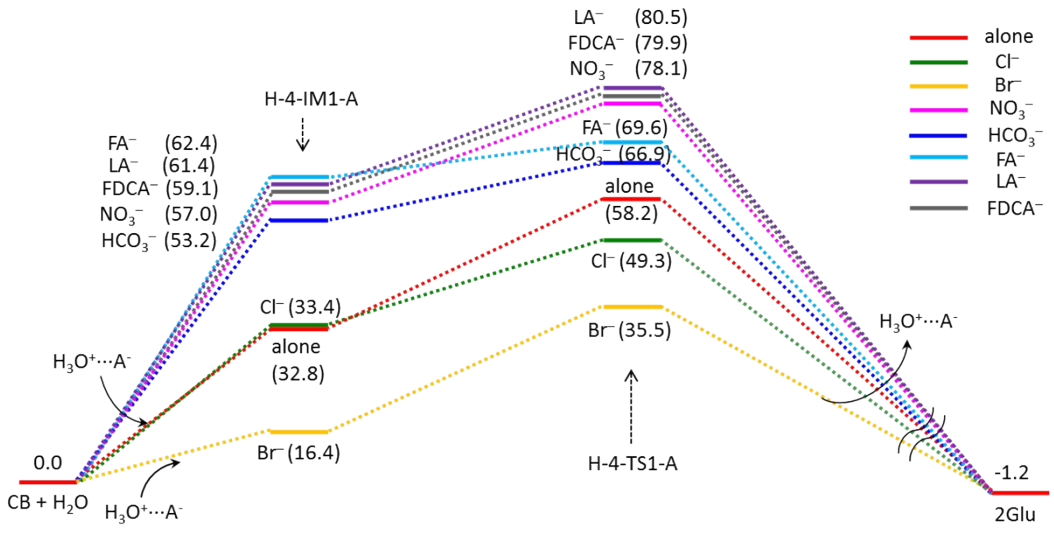


Figure S11. The geometric structures with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the protonated glycosyl-HMF in the presence of H_3O^+ alone and in the presence of H_3O^+ together with the counterpart anion (A^- = Cl^-, Br^-, NO_3^-, HCO_3–, FA^-, LA^-, and $FDCA^-$) in aqueous solution. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

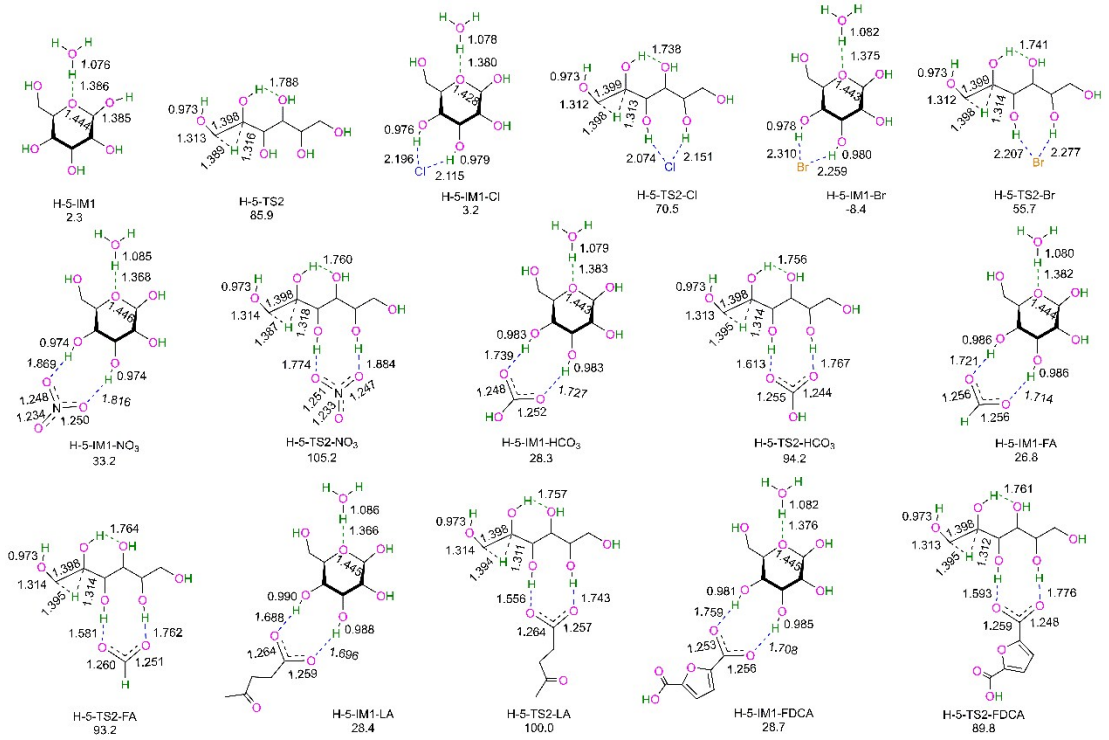


(a)

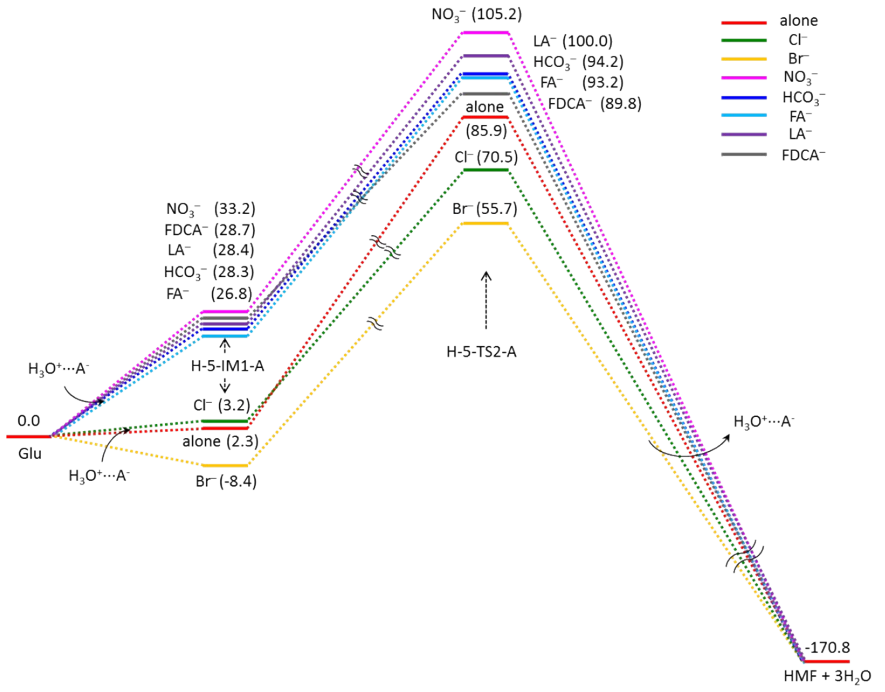


(b)

Figure S12. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the hydrolysis of *β*-cellobiose (CB) to glucose (Glu) in the presence of H_3O^+ alone and and in the presence of H_3O^+ together with the counterpart anion (A^- = Cl^-, Br^-, NO_3^-, HCO_3^-, FA^-, LA^-, and $FDCA^-$) in aqueous solution. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

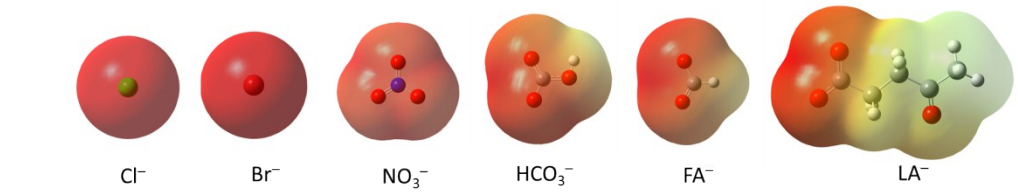


(a)

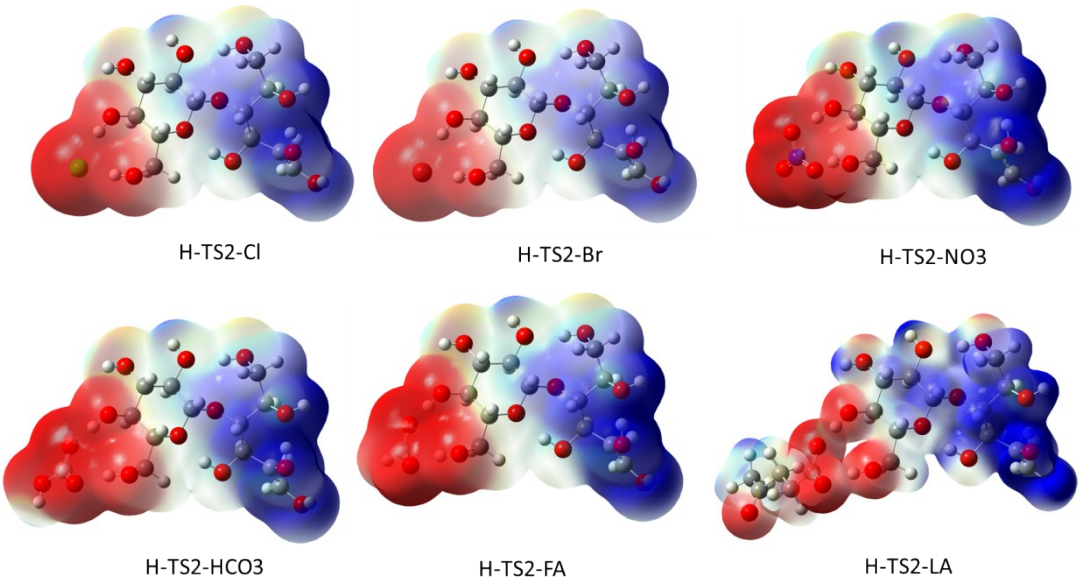


(b)

Figure S13. The geometric structures (a) and the schematic energy diagrams (b) with the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to the reactants for the conversion of *β*-D-glucopyranose (Glu) to 5-hydroxymethylfurfural (HMF) in the presence of H_3O^+ alone and in the presence of H_3O^+ together with the counterpart anion (A^- = Cl^-, Br^-, NO_3^-, HCO_3^-, FA^-, LA^-, and $FDCA^-$) in aqueous solution. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.



(a)



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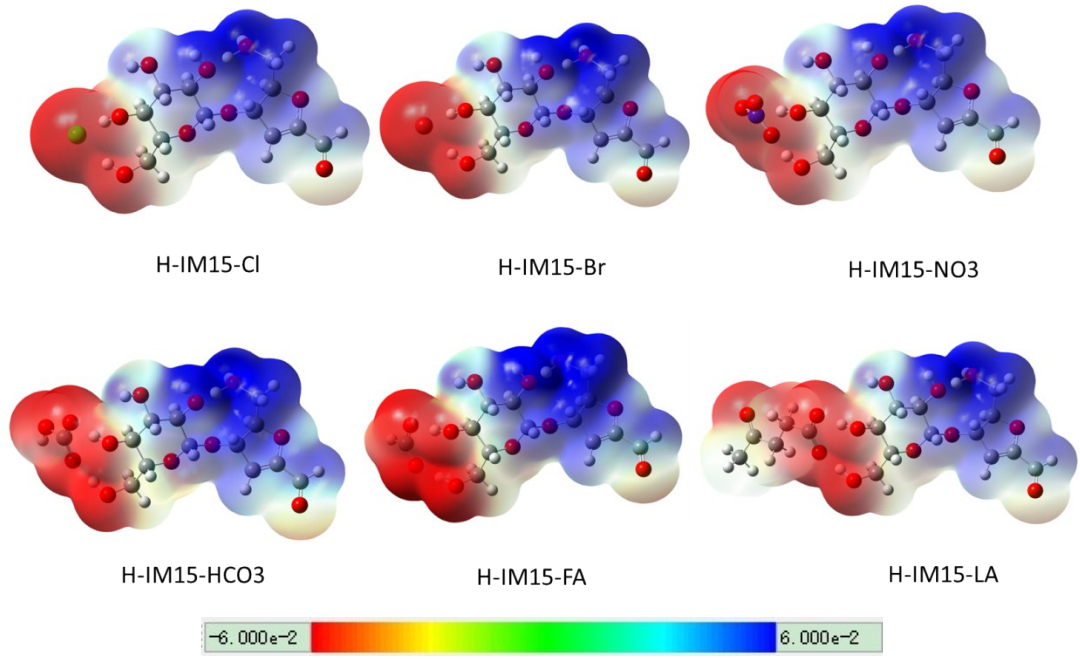

(c)

Figure S14. Electrostatic potential (ESP) on the 0.001 au molecular surface. (a) counterpart anion. (b) TOF-determining transition state (TDTS) together with the counterpart anion. (c) glycosyl-HMF together with the counterpart anion.

Table S1. The reactivity index analysis from Parr functions for the O and H atom sites of *β*-cellobiose (CB2). P_{κ}^{-} and P_{κ}^{+} stand for nucleophilic Parr functions and electrophilic Parr functions, respectively. N_{κ} and ω_{κ} (eV) stand for local nucleophilic index and local electrophilic index, respectively.

O atom sites	O1	O2	O3	O5	O6	O1′	O2′	O3′	O4′	O5′	O6′
P_{κ}^{-}	0.01	0.07	0.05	0.52	0.03	0.04	0.00	0.00	0.00	0.00	0.00
N_{κ}	0.01	0.09	0.06	0.69	0.04	0.06	0.00	0.00	0.00	0.00	0.00
H atom sites	O1H1	O2H2	O3H3		O6H6		O2′H2′	O3′H3′	O4′H4′		O6′H6′
P_{κ}^{+}	0.00	0.00	–0.03		0.00		0.00	0.01	0.13		1.10
ω_{κ}	0.00	0.00	–0.04		0.00		0.00	0.01	0.14		1.20

The reactivity index analysis from Parr functions indicated that the O5 atom was more electron-rich at the reducing end of *β*-cellobiose, with the local nucleophilic index of 0.69 eV.

Table S2. The molar volume (V, $cm^3\ mol^{-1}$) of counter anions (A^-), the relative entropies (ΔS, $J\ mol^{-1}\ K^{-1}$), relative enthalpies (ΔH, $kJ\ mol^{-1}$) and relative Gibbs free energies (ΔG, $kJ\ mol^{-1}$) of TOF-determining transition state (TDTS), and rate constants (k, $s^{-1}\ mol^{-2}\ dm^6$) for the conversion of β-cellobiose to glucose and 5-hydroxymethylfurfural (CB → Glu + HMF + $2H_2O$) in the absence of the catalyst and in the presence of H_3O^+ together with the counterpart anion (A^- = Cl^-, Br^-, NO_3^-, HCO_3^-, FA^-, LA^-, and $FDCA^-$) in aqueous solution.

counter anion (A^-)	V, $cm^3\ mol^{-1}$	TDTS (H-TS2-A + H_2O)			k, $s^{-1}\ mol^{-2}\ dm^6$ 293 K ~ 493 K
		ΔS	ΔH	ΔG	
alone		5.0	96.7	94.3	$k_{C/H} = 5.111\times10^{13}\exp(-97,623/RT)$
Cl^-	33.2	-64.3	52.3	83.9	$k_{C/H\text{-}Cl} = 1.168\times10^{10}\exp(-52,914/RT)$
Br^-	30.7	-75.8	39.2	76.6	$k_{C/H\text{-}Br} = 3.135\times10^{9}\exp(-40,146/RT)$
NO_3^-	47.1	-109.5	67.7	112.8	$k_{C/H\text{-}NO_3} = 6.625\times10^{7}\exp(-69,225/RT)$
HCO_3^-	42.5	-102.8	56.3	107.0	$k_{C/H\text{-}HCO_3} = 1.462\times10^{6}\exp(-44,847/RT)$
FA^-	32.2	-108.2	53.8	107.1	$k_{C/H\text{-}FA} = 3.568\times10^{7}\exp(-53,305/RT)$
LA^-	78.6	-147.0	52.9	125.3	$k_{C/H\text{-}LA} = 4.504\times10^{5}\exp(-52,702/RT)$
$FDCA^-$	98.1	-124.9	57.4	118.9	$k_{C/H\text{-}FDCA} = 6.206\times10^{6}\exp(-57,066/RT)$

Notes:

The molar volume (V, $cm^3\ mol^{-1}$) of counter anions increases as

$Br^- < FA^- < Cl^- < HCO_3 < NO_3^- < LA^- < FDCA^-$.

The $-\Delta S$ increases as $Cl^- < Br^- < HCO_3^- < FA^- < NO_3^- < FDCA^- < LA^-$.

The ΔH increases as $Br^- < Cl^- < LA^- < FA^- < HCO_3^- < FDCA^- < NO_3^-$.

The ΔG increases as $Br^- < Cl^- < HCO_3^- < FA^- < FDCA^- < NO_3^- < LA^-$.

Over the 293 – 365 K temperature range, the rate constants (k) decrease as $k_{C/H\text{-}Br} > k_{C/H\text{-}Cl} \gg k_{C/H\text{-}FA} > k_{C/H\text{-}HCO3} > k_{C/H} > k_{C/H\text{-}FDCA} > k_{C/H\text{-}LA} > k_{C/H\text{-}NO3}$.

Over the 365 – 398 K temperature range, the rate constants (k) decrease as $k_{C/H\text{-}Br} > k_{C/H\text{-}Cl} \gg k_{C/H\text{-}FA} > k_{C/H} > k_{C/H\text{-}HCO3} > k_{C/H\text{-}FDCA} > k_{C/H\text{-}LA} > k_{C/H\text{-}NO3}$.

Over the 398 – 493 K temperature range, the rate constants (k) decrease as $k_{C/H\text{-}Br} > k_{C/H\text{-}Cl} \gg k_{C/H\text{-}FA} > k_{C/H} > k_{C/H\text{-}HCO3} > k_{C/H\text{-}FDCA} > k_{C/H\text{-}NO3} > k_{C/H\text{-}LA}$.

Table S3. The molar volume (V, $cm^3\ mol^{-1}$) of counter anions (A^-), the relative entropies (ΔS, $J\ mol^{-1}\ K^{-1}$), relative enthalpies (ΔH, $kJ\ mol^{-1}$) and relative Gibbs free energies (ΔG, $kJ\ mol^{-1}$) of TOF-determining transition state (TDTS), and rate constants (k, $s^{-1}\ mol^{-2}\ dm^6$) for the hydrolysis of β-cellobiose to glucose (CB + H_2O → 2Glu) in the absence of the catalyst and in the presence of H_3O^+ together with the counterpart anion (A^- = Cl^-, Br^-, NO_3^-, HCO_3^-, FA^-, LA^-, and $FDCA^-$) in aqueous solution.

counter anion (A^-)	V, $cm^3\ mol^{-1}$	TDTS (H-4-TS1-A + H_2O)			k, $s^{-1}\ mol^{-2}\ dm^6$ 293 K ~ 493 K
		ΔS	ΔH	ΔG	
alone		9.6	63.0	58.2	$k_{C/G} = 5.838\times10^{13}\exp(-62,834/RT)$
Cl^-	33.2	-75.3	12.2	49.3	$k_{C/G\text{-}Cl} = 4.091\times10^{9}\exp(-14,706/RT)$
Br^-	30.7	-74.5	-1.2	35.5	$k_{C/G\text{-}Br} = 5.057\times109\exp(-1,708/RT)$
NO_3^-	47.1	-122.2	26.7	78.1	$k_{C/G\text{-}NO_3} = 1.014\times10^{7}\exp(-27,854/RT)$
HCO_3^-	42.5	-109.4	13.0	66.9	$k_{C/G\text{-}HCO_3} = 4.725\times10^{7}\exp(-14,129/RT)$
FA^-	32.2	-118.8	11.1	69.6	$k_{C/G\text{-}FA} = 1.658\times10^{7}\exp(-12,472/RT)$
LA^-	78.6	-147.9	7.6	80.5	$k_{C/G\text{-}LA} = 5.176\times10^{5}\exp(-9,181/RT)$
$FDCA^-$	98.1	-134.5	13.6	79.9	$k_{C/G\text{-}FDCA} = 2.453\times10^{6}\exp(-14,937/RT)$

Notes:

The molar volume (V, $cm^3\ mol^{-1}$) of counter anions increases as

$Br^- < FA^- < Cl^- < HCO_3^- < NO_3^- < LA^- < FDCA^-$.

$-\Delta S$ increases as $Br^- < Cl^- < HCO_3^- < FA^- < NO_3^- < FDCA^- < LA^-$.

ΔH increases as $Br^- < LA^- < FA^- < Cl^- < HCO_3^- < FDCA^- < NO_3^-$.

ΔG increases as $Br^- < Cl^- < HCO_3^- < FA^- < NO_3^- < FDCA^- < LA^-$.

Over the 293 – 338 K temperature range, the rate constants (k) decrease as $k_{C/G\text{-}Br} > k_{C/G\text{-}Cl} > k_{C/G\text{-}HCO3} > k_{C/G\text{-}FA} > k_{C/G\text{-}LA} > k_{C/G\text{-}FDCA} > k_{C/G} > k_{C/G\text{-}NO3}$.

Over the 338 – 433 K temperature range, the rate constants (k) decrease as $k_{C/G\text{-}Br} > k_{C/G\text{-}Cl} > k_{C/G\text{-}HCO3} > k_{C/G\text{-}FA} > k_{C/G\text{-}LA} > k_{C/G} > k_{C/G\text{-}FDCA} > k_{C/G\text{-}NO3}$.

Over the 433 – 493 K temperature range, the rate constants (k) decrease as $k_{C/G\text{-}Br} > k_{C/G\text{-}Cl} > k_{C/G\text{-}HCO3} > k_{C/G\text{-}FA} > k_{C/G} > k_{C/G\text{-}FDCA} > k_{C/G\text{-}LA} > k_{C/G\text{-}NO3}$.

Table S4. The molar volume (V, $cm^3\ mol^{-1}$) of counter anions (A^-), the relative entropies (ΔS, $J\ mol^{-1}\ K^{-1}$), relative enthalpies (ΔH, $kJ\ mol^{-1}$) and relative Gibbs free energies (ΔG, $kJ\ mol^{-1}$) of TOF-determining transition state (TDTS), and rate constants (k, $s^{-1}\ mol^{-2}\ dm^6$) for the conversion of β-D-glucopyranose to 5-hydroxymethylfurfural (Glu → HMF + $3H_2O$) in the absence of the catalyst and in the presence of H_3O^+ together with the counterpart anion (A^- = Cl^-, Br^-, NO_3^-, HCO_3^-, FA^-, LA^-, and $FDCA^-$) in aqueous solution.

counter anion (A^-)	V, $cm^3\ mol^{-1}$	TDTS (H-5-TS2-A + H_2O)			k, $s^{-1}\ mol^{-2}\ dm^6$ 293 K ~ 493 K
		ΔS	ΔH	ΔG	
alone		-8.4	81.7	85.9	$k_{G/H} = 1.557\times10^{13}\exp(-84,578/RT)$
Cl^-	33.2	-73.8	34.2	70.5	$k_{G/H\text{-}Cl} = 4.458\times10^{9}\exp(-34,823/RT)$
Br^-	30.7	-70.9	20.8	55.7	$k_{G/H\text{-}Br} = 5.645\times10^{9}\exp(-21,287/RT)$
NO_3^-	47.1	-111.5	50.3	105.2	$k_{G/H\text{-}NO_3} = 3.022\times10^{7}\exp(-49,408/RT)$
HCO_3^-	42.5	-117.2	36.4	94.2	$k_{G/H\text{-}HCO_3} = 2.307\times10^{7}\exp(-35,228/RT)$
FA^-	32.2	-119.8	34.1	93.2	$k_{G/H\text{-}FA} = 1.185\times10^{7}\exp(-33,547/RT)$
LA^-	78.6	-140.5	30.8	100.0	$k_{G/H\text{-}LA} = 1.026\times10^{6}\exp(-30,322/RT)$
$FDCA^-$	98.1	-107.7	36.8	89.8	$k_{G/H\text{-}FDCA} = 4.893\times10^{7}\exp(-36,009/RT)$

Notes:

The molar volume (V, $cm^3\ mol^{-1}$) of counter anions increases as

$Br^- < FA^- < Cl^- < HCO_3 < NO_3^- < LA^- < FDCA^-$.

$-\Delta S$ increases as $Br^- < Cl^- < FDCA^- < NO_3^- < HCO_3^- < FA^- < LA^-$.

ΔH increases as $Br^- < LA^- < FA^- < Cl^- < HCO_3^- < FDCA^- < NO_3^-$.

ΔG increases as $Br^- < Cl^- < FDCA^- < FA^- < HCO_3^- < LA^- < NO_3^-$.

Over the 293 – 327 K temperature range, the rate constants (k) decrease as $k_{G/H\text{-}Br} > k_{G/H\text{-}Cl} \gg k_{G/H\text{-}FDCA} > k_{G/H\text{-}HCO3} > k_{G/H\text{-}FA} > k_{G/H\text{-}LA} > k_{G/H} > k_{G/H\text{-}NO3}$.

Over the 227 – 360 K temperature range, the rate constants (k) decrease as $k_{G/H\text{-}Br} > k_{G/H\text{-}Cl} \gg k_{G/H\text{-}FDCA} > k_{G/H\text{-}HCO3} > k_{G/H\text{-}FA} > k_{G/H} > k_{G/H\text{-}LA} > k_{G/H\text{-}NO3}$.

Over the 360 – 493 K temperature range, the rate constants (k) decrease as $k_{G/H\text{-}Br} > k_{G/H\text{-}Cl} \gg k_{G/H} > k_{G/H\text{-}FDCA} > k_{G/H\text{-}HCO3} > k_{G/H\text{-}FA} > k_{G/H\text{-}LA} > k_{G/H\text{-}NO3}$.

Table S5. The rate constant (k), the TOF determining transition state (TDTS) and the TOF determining intermediate (TDI), the relative Gibbs free energy (G, kJ mol^{-1}) relative to the reactants, the energy height of the highest point (EHHP), the highest energy barrier (HEB), and the energy height of lowest point (EHLP) for the whole conversion of β-cellobiose (CB2) to 5-hydroxymethylfurfural (HMF).

path	TDI (G_{TDI}, kJ mol^{-1})	TDTS (G_{TDTS}, kJ mol^{-1})	EHHP (kJ mol^{-1})	HEB (kJ mol^{-1})	EHLP (kJ mol^{-1})	k, s^{-1} mol^{-1} dm^3
C/H	CB2 + H_3O^+ 0.0	H-TS2 + H_2O 94.3	H-TS2 + H_2O 94.3	H-IM4 → H-TS2 77.9	HMFH -114.1	$k_{C/H} = 5.111\times10^{13}\exp(-97,623/RT)$
C/G/H	Glu + H_3O^+ -1.2	H-5-TS2 + H_2O 84.7	H-5-TS2 + H_2O 84.7	H-6b-IM3 → H-6b-TS3 63.3	HMFH-IM1 -78.5	$k_{G/H} = 1.557\times10^{13}\exp(-84,578/RT)$

Table S6. The rate constant (k), the TOF determining transition state (TDTS) and the TOF determining intermediate (TDI), the relative Gibbs free energy (G, kJ mol^{-1}) relative to the reactants, the energy height of the highest point (EHHP), the highest energy barrier (HEB), and the energy height of lowest point (EHLP) for the aldose-ketose isomerization of β-cellobiose (CB2) and glucose (Glu) to cellobiulose (CBU) and β-D-fructofuranoses (β-FF), respectively.

isomerization	TDI (G_{TDI}, kJ mol^{-1})	TDTS (G_{TDTS}, kJ mol^{-1})	EHHP (kJ mol^{-1})	HEB (kJ mol^{-1})	EHLP (kJ mol^{-1})	k, s^{-1} mol^{-1} dm^3
CB → CBU	CB2 + H_3O^+ 0.0	H-TS2 + H_2O 94.3	H-TS2 + H_2O 94.3	H-IM4 → H-TS2 77.9	CB2 + H_3O^+ 0.0	$k_{C/H} = 5.111\times10^{13}\exp(-97,623/RT)$
Glu → β-FF	Glu + H_3O^+ 0.0	H-5-TS2 + H_2O 85.9	H-5-TS2 + H_2O 85.9	H-5-IM4 → H-5-TS2 47.6	Glu + H_3O^+ 0.0	$k_{G/H} = 1.557\times10^{13}\exp(-84,578/RT)$

Table S7. The rate constant (k), the TOF determining transition state (TDTS) and the TOF determining intermediate (TDI), the relative Gibbs free energy (G, kJ mol^{-1}) relative to the reactants, the energy height of the highest point (EHHP), the highest energy barrier (HEB), and the energy height of lowest point (EHLP) for the glucosidic bond cleavage.

glucosidic bond cleavage	TDI (G_{TDI}, kJ mol^{-1})	TDTS (G_{TDTS}, kJ mol^{-1})	EHHP (kJ mol^{-1})	HEB (kJ mol^{-1})	EHLP (kJ mol^{-1})	k, s^{-1} mol^{-1} dm^3
CB → 2Glu	Glu + H_3O^+ 0.0	H-4-TS1 + H_2O 58.2	H-4-TS1 + H_2O 58.2	H-4-IM3 → H-4-TS2 50.0	H-4-IM3 + Glu -4.6	$k_{C/G} = 5.838\times10^{13}\exp(-62,834/RT)$
CBU → Glu + β-FF	CBU + H_3O^+ 0.0	CBU-H-TS1 + H_2O 62.8	CBU-H-TS1 + H_2O 62.8	CBUH → CBU-H-TS1 28.5	H-4-IM3 + β-FF -15.5	$k_{CBU/F} = 9.161\times10^{12}\exp(-59,835/RT)$
Glycosyl-HMF → Glu + HMFH	Glycosyl-HMF + H_3O^+ 0.0	H-TS10 + H_2O 37.4	H-TS10 + H_2O 37.4	H-IM15 → H-TS10 60.9	Glu + HMFH -67.4	$k_{GH/H} = 1.365\times10^{12}\exp(-24,732/RT)$

Table S8. The rate constant (k), the TOF determining transition state (TDTS) and the TOF determining intermediate (TDI), the relative Gibbs free energy (G, kJ mol^{-1}) relative to the reactants, the energy height of the highest point (EHHP), the highest energy barrier (HEB), and the energy height of lowest point (EHLP) for the dehydration of cellobiulose (CBU) and β-D-fructofuranoses (β-FF), respectively.

dehydration	TDI (G_{TDI}, kJ mol^{-1})	TDTS (G_{TDTS}, kJ mol^{-1})	EHHP (kJ mol^{-1})	HEB (kJ mol^{-1})	EHLP (kJ mol^{-1})	k, s^{-1} mol^{-1} dm^3
CBU → Glycosyl-HMF	CBU + H_3O^+ 0.0	H-TS6a + H_2O 72.3	H-TS6a + H_2O 72.3	H-IM9a → H-TS6a 66.7		$k_{CBU/GH} = 2.014\times10^{15}\exp(-88,478/RT)$
β-FF → HMF	β-FF + H_3O^+ 0.0	H-6b-TS3 + H_2O 68.2	H-6b-TS3 + H_2O 68.2	H-6b-IM3 → H-6b-TS3 63.3		$k_{F/H} = 1.423\times10^{16}\exp(-94,572/RT)$

Table S9. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) relative to CB1 for seven configurations of β-cellobiose at M06-2x/6-311++G(d,p) level in aqueous solution.

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
CB1	0.37639	-1297.55529	0.32492	-1297.60677	0.0	0.0
CB2	0.37669	-1297.55845	0.32506	-1297.61007	-8.3	-8.7
CB3	0.37588	-1297.55523	0.32327	-1297.60784	0.1	-2.8
CB4	0.37571	-1297.55575	0.32302	-1297.60844	-1.2	-4.4
CB5	0.37564	-1297.54442	0.32525	-1297.59482	28.5	31.4
CB6	0.37730	-1297.55541	0.32624	-1297.60646	-0.3	0.8
CB7	0.377101	-1297.554589	0.326093	-1297.605597	1.8	3.1

Table S10. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the conversion of *β*-cellobiose into both glucose and HMF (CB → Glu + HMF + 2H_2O) in the absence of catalyst and H_2O at M06-2X/6-311++G(d,p) level in aqueous media under experimental temperature and pressure (493.0 K and 24.3 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
CB2	0.37669	-1297.55845	0.27153	-1297.66360	0.0	0.0
H_2O	0.02129	-76.41355	-0.00607	-76.44091		
u-TS1	0.37111	-1297.48531	0.26653	-1297.58989	192.0	193.5
u-IM2	0.37260	-1297.53519	0.26289	-1297.64491	61.1	49.1
u-TS2	0.36696	-1297.42612	0.25826	-1297.53481	347.4	338.1
u-IM3	0.37181	-1297.53745	0.26177	-1297.64749	55.1	42.3
u-TS3	0.36598	-1297.43920	0.25610	-1297.54908	313.1	300.7
u-IM4	0.37348	-1297.54605	0.26419	-1297.65535	32.6	21.7
u-TS4	0.37052	-1297.48127	0.26455	-1297.58724	202.6	200.5
u-TS4a	0.36890	-1297.47457	0.26166	-1297.58181	220.2	214.8
u-IM5 (CBU)	0.37527	-1297.54943	0.26573	-1297.65897	23.7	12.2
u-TS5	0.36745	-1297.45731	0.25381	-1297.57094	265.5	243.3
u-IM6	0.34619	-1221.11552	0.24164	-1221.22008		
u-IM6 + H_2O	0.36748	-1297.52907	0.23557	-1297.66099	77.1	6.9
u-TS6	0.33990	-1221.01405	0.23595	-1221.11800		
u-TS6 + H_2O	0.36119	-1297.42760	0.22988	-1297.55890	343.5	274.9
u-IM7	0.34650	-1221.11988	0.24138	-1221.22500		
u-IM7 + H_2O	0.36779	-1297.53343	0.23531	-1297.66590	65.7	-6.0
u-TS7	0.33961	-1221.03623	0.23482	-1221.14101		
u-TS7 + H_2O	0.36090	-1297.44978	0.22876	-1297.58192	285.3	214.4
u-TS7a	0.34147	-1221.07690	0.24078	-1221.17759		
u-TS7a + H_2O	0.36276	-1297.49046	0.23471	-1297.61850	178.5	118.4
u-IM8	0.34142	-1221.11613	0.22974	-1221.22781		
u-IM8 + H_2O	0.36271	-1297.52969	0.22367	-1297.66872	75.5	-13.4
u-IM9 (glycosyl-HMF)	0.31708	-1144.69805	0.21556	-1144.79956		
u-IM9 + 2H_2O	0.35966	-1297.52515	0.20343	-1297.68137	87.4	-46.7
u-TS8	0.33307	-1221.05663	0.22393	-1221.16577		
u-TS8 + H2O	0.35436	-1297.47019	0.21786	-1297.60668	231.7	149.5
Glu	0.19958	-686.98102	0.12813	-687.05247	□	□
HMF	0.11341	-457.73550	0.05413	-457.79478	□	□
Glu + HMF + 2H_2O	0.35557	-1297.54362	0.17012	-1297.72907	38.9	-171.9

Table S11. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the conversion of *β*-cellobiose into both glucose and HMF (CB → Glu + HMF + 2H_2O) in the presence of explicit H_2O at M06-2X/6-311++G(d,p) level in aqueous media under experimental temperature and pressure (493.0 K and 24.3 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
CB2	0.37669	-1297.55845	0.27153	-1297.66360	0.0	0.0
H_2O	0.02129	-76.41355	-0.00607	-76.44091		
CB2 + H_2O	0.39798	-1373.97200	0.26547	-1374.10450	0.0	0.0
W-IM1	0.40099	-1373.97588	0.28497	-1374.09191	-10.2	33.1
W-TS1	0.39538	-1373.93696	0.28515	-1374.04719	92.0	150.5
W-IM2	0.39766	-1373.95365	0.27957	-1374.07174	48.2	86.0
W-TS2a	0.39559	-1373.88972	0.28100	-1374.00430	216.0	263.1
2W-TS2a	0.41692	-1450.32252	0.29522	-1450.44421		
2W-TS2a - H_2O	0.39563	-1373.90897	0.30129	-1374.00331	165.5	265.7
W-IM3a	0.39776	-1373.94786	0.28032	-1374.06531	63.4	102.9
W-TS3a	0.39535	-1373.89648	0.28122	-1374.01061	198.3	246.5
W-TS2b	0.39250	-1373.90828	0.27725	-1374.02353	167.3	212.6
W-IM3	0.39799	-1373.96551	0.27973	-1374.08377	17.0	54.4
W-TS3	0.39359	-1373.92842	0.28027	-1374.04174	114.4	164.8
W-IM4	0.40034	-1373.96653	0.28416	-1374.08271	14.4	57.2
W-TS4	0.39166	-1373.88531	0.27355	-1374.00342	227.6	265.4
W-IM5	0.37089	-1297.53041	0.25762	-1297.64368		
W-IM5 + H_2O	0.39218	-1373.94396	0.25156	-1374.08459	73.6	52.3
W-TS5	0.36820	-1297.49260	0.25794	-1297.60285		
W-TS5 + H_2O	0.38949	-1373.90615	0.25188	-1374.04376	172.9	159.5
u-IM8	0.34142	-1221.11613	0.22974	-1221.22781		
u-IM8 + H_2O	0.36271	-1297.52969	0.22367	-1297.66872	75.5	-13.4
u-IM9 (glycosyl-HMF)	0.31708	-1144.69805	0.21556	-1144.79956		
u-IM9 + 2H_2O	0.35966	-1297.52515	0.20343	-1297.68137	87.4	-46.7
u-TS8	0.33307	-1221.05663	0.22393	-1221.16577		
u-TS8 + H_2O	0.35436	-1297.47019	0.21786	-1297.60668	231.7	149.5
Glu	0.19958	-686.98102	0.12813	-687.05247		
HMF	0.11341	-457.73550	0.05413	-457.79478		
Glu + HMF + 2H_2O	0.35557	-1297.54362	0.17012	-1297.72907	38.9	-171.9

Table S12. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the conversion of *β*-cellobiose into both glucose and HMF (CB → Glu + HMF + 2H_2O) catalyzed by H_3O^+ at M06-2X/6-311++G(d,p) level in aqueous media under experimental temperature and pressure (493.0 K and 24.3 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
CB2	0.37669	-1297.55845	0.27153	-1297.66360		
H_3O^+	0.03310	-76.80965	0.00337	-76.83939		
H_2O	0.02129	-76.41355	-0.00607	-76.44091		
CB2 + H_3O^+	0.40979	-1374.36810	0.27490	-1374.50298	0.0	0.0
H-IM1	0.413956	-1374.387783	0.300823	-1374.500916	-51.7	5.4
H-IM2	0.390283	-1297.950817	0.285309	-1298.055792		
H-IM2 + H_2O	0.41157	-1374.364369	0.279243	-1374.4967	9.8	16.5
H-TS1	0.408099	-1374.366894	0.294287	-1374.480706	3.2	58.5
H-IM3	0.410423	-1374.375077	0.294739	-1374.490762	-18.3	32.1
H-IM4	0.38602	-1297.94236	0.27666	-1298.05171		
H-IM4 + H_2O	0.40731	-1374.35591	0.27060	-1374.49262	32.0	27.2
H-TS2	0.38231	-1297.91890	0.27505	-1298.02616		
H-TS2 + H_2O	0.40361	-1374.33245	0.26899	-1374.46707	93.6	94.3
H-TS2a	0.407025	-1374.342965	0.289989	-1374.460001	66.0	112.8
H-IM3a	0.409938	-1374.3771	0.292124	-1374.494914	-23.6	21.2
H-IM5	0.38713	-1297.94740	0.28033	-1298.05420		
H-IM5 + H_2O	0.40842	-1374.36096	0.27427	-1374.49510	18.8	20.7
H-TS3	0.41117	-1374.36803	0.29379	-1374.48541	0.2	46.1
H-IM6	0.41219	-1374.38063	0.29629	-1374.49653	-32.9	16.9
CBU	0.37527	-1297.54943	0.26573	-1297.65897		
CBU + H_3O^+	0.40837	-1374.35908	0.26910	-1374.49835	23.7	12.2
H-IM7	0.41137	-1374.38410	0.29474	-1374.50074	-42.0	5.9
H-TS4a	0.40974	-1374.35846	0.29150	-1374.47670	25.3	69.0
H-IM8a	0.38425	-1297.94122	0.27101	-1298.05446		
H-IM8a + H_2O	0.40554	-1374.35478	0.26495	-1374.49537	35.0	20.0
H-TS5a	0.37884	-1297.92120	0.26770	-1298.03234		
H-TS5a + H_2O	0.40013	-1374.33476	0.26164	-1374.47325	87.5	78.1
H-IM9a	0.38301	-1297.94305	0.27078	-1298.05528		
H-IM9a + H_2O	0.40430	-1374.35660	0.26471	-1374.49619	30.2	17.8
H-TS6a	0.38057	-1297.91595	0.26662	-1298.02990		
H-TS6a + H_2O	0.40186	-1374.32950	0.26055	-1374.47081	101.3	84.5
H-IM7b	0.38740	-1297.94649	0.27773	-1298.05616		

H-IM7b + H_2O	0.40869	-1374.36004	0.27166	-1374.49707	21.2	15.5

Continued from **Table S12**

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
H-TS4b	0.38521	-1297.93816	0.27358	-1298.04979		
H-TS4b + H_2O	0.40650	-1374.35171	0.26751	-1374.49070	43.0	32.3
H-IM8b	0.35941	-1221.51936	0.25536	-1221.62341		
H-IM8b + $2H_2O$	0.40199	-1374.34647	0.24323	-1374.50522	56.8	-5.9
H-TS5b	0.35587	-1221.49576	0.25330	-1221.59833		
H-TS5b + $2H_2O$	0.39845	-1374.32287	0.24117	-1374.48014	118.8	60.0
H-IM9b	0.35988	-1221.51283	0.25494	-1221.61777		
H-IM9b + $2H_2O$	0.40247	-1374.33993	0.24280	-1374.49959	74.0	8.9
H-TS6b	0.35560	-1221.51230	0.25357	-1221.61433		
H-TS6b + $2H_2O$	0.39818	-1374.33940	0.24144	-1374.49614	75.3	18.0
H-IM10b	0.35876	-1221.52243	0.25500	-1221.62619		
H-IM10b + $2H_2O$	0.40134	-1374.34954	0.24287	-1374.50800	48.7	-13.2
H-TS7b	0.35047	-1221.45895	0.24202	-1221.56740		
H-TS7b + $2H_2O$	0.39306	-1374.28605	0.22989	-1374.44922	215.4	141.2
H-IM11b	0.33050	-1145.09339	0.22895	-1145.19494		
H-IM11b + $3H_2O$	0.39437	-1374.33404	0.21075	-1374.51766	89.4	-38.5
H-TS8b	0.32515	-1145.03604	0.22513	-1145.13607		
H-TS8b + $3H_2O$	0.38903	-1374.27670	0.20693	-1374.45879	240.0	116.0
H-IM12a	0.33092	-1145.08918	0.23064	-1145.18946		
H-IM12a + $3H_2O$	0.39479	-1374.32983	0.21244	-1374.51218	100.5	-24.2
H-IM13a	0.35601	-1221.52212	0.24861	-1221.62952		
H-IM13a + $2H_2O$	0.39860	-1374.34922	0.23648	-1374.51134	49.6	-21.9
H-TS9b	0.35026	-1221.49909	0.24251	-1221.60684		
H-TS9b + $2H_2O$	0.39284	-1374.32619	0.23037	-1374.48865	110.0	37.6
glycosyl-HMF	0.31708	-1144.69805	0.21556	-1144.79956		
glycosyl-HMF + H_3O^+ + $2H_2O$	0.39276	-1374.33480	0.20680	-1374.52076	87.4	-46.7
H-IM14	0.35427	-1221.53457	0.24960	-1221.63924		
H-IM14 + $2H_2O$	0.39685	-1374.36168	0.23747	-1374.52106	16.9	-47.5
H-IM15	0.32881	-1145.10883	0.23063	-1145.20701		
H-IM15 + $3H_2O$	0.39269	-1374.34948	0.21243	-1374.52974	48.9	-70.2
H-TS10	0.32800	-1145.08485	0.22905	-1145.18380		
H-TS10 + $3H_2O$	0.39187	-1374.32551	0.21086	-1374.50652	111.8	-9.3
H-IM16	0.33007	-1145.09016	0.22819	-1145.19203		
H-IM16 + $3H_2O$	0.39394	-1374.33082	0.20999	-1374.51476	97.9	-30.9
H-TS11	0.32818	-1145.08692	0.22712	-1145.18799		
H-TS11 + $3H_2O$	0.39205	-1374.32758	0.20892	-1374.51071	106.4	-20.3

Glu	0.19958	-686.98102	0.12813	-687.05247		

Continued from **Table S12**

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
HMFH	0.12591	-458.11140	0.06607	-458.17123		
Glu + HMFH + $3H_2O$	0.38936	-1374.33307	0.17600	-1374.54643	92.0	-114.1
H-TS10a	0.35350	-1221.50538	0.24485	-1221.61403		
H-TS10a + $2H_2O$	0.39609	-1374.33249	0.23272	-1374.49585	93.5	18.7
HMFH-IM1	0.15035	-534.52752	0.07931	-534.59857		
Glu + HMFH-IM1 + $2H_2O$	0.39251	-1374.33565	0.19530	-1374.53286	85.2	-78.4
HMFH-TS1	0.14624	-534.51895	0.07842	-534.58677		
Glu + HMFH-TS1 + $2H_2O$	0.38840	-1374.32708	0.19441	-1374.52106	107.7	-47.5
HMF	0.11341	-457.73550	0.05413	-457.79478		
Glu + HMF + H_3O^+ + $2H_2O$	0.38868	-1374.35327	0.17349	-1374.56846	38.9	-171.9

Table S13. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the hydrolysis of *β*-cellobiose (CB2) to glucose (Glu) (CB + H_2O→ 2Glu) in the absence of catalyst at M06-2X/6-311++G(d,p) level in aqueous media under experimental temperature and pressure (493.0 K and 24.3 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
CB2	0.37669	-1297.55845	0.27153	-1297.66360		
H_2O	0.02129	-76.41355	-0.00607	-76.44091		
CB + H_2O	0.39798	-1373.97200	0.26547	-1374.10450	0.0	0.0
u4-TS1	0.39598	-1373.88648	0.28056	-1374.00191	224.5	269.4
Glu	0.19958	-686.98102	0.12813	-687.05247		
2Glu	0.39916	-1373.96204	0.25625	-1374.10494	26.2	-1.2

Table S14. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the hydrolysis of *β*-cellobiose (CB2) to glucose (Glu) (CB + H_2O→ 2Glu) catalyzed by H_3O^+ at M06-2X/6-311++G(d,p) level in aqueous media under experimental temperature and pressure (493.0 K and 24.3 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
CB2	0.37669	-1297.55845	0.27153	-1297.66360		
H_3O^+	0.03310	-76.80965	0.00337	-76.83939		
H_2O	0.02129	-76.41355	-0.00607	-76.44091		
CB2 + H_3O^+ + H_2O	0.43108	-1450.78165	0.26884	-1450.94389	0.0	0.0
H-4-IM1	0.38975	-1297.94325	0.28341	-1298.04959		
H-4-IM1 + 2H_2O	0.43233	-1450.77035	0.27128	-1450.93141	29.7	32.8
H-4-TS1	0.38717	-1297.93196	0.27924	-1298.03990		
H-4-TS1 + 2H_2O	0.42975	-1450.75907	0.26711	-1450.92171	59.3	58.2
H-4-IM2	0.38605	-1297.93425	0.27360	-1298.04670		
H-4-IM2 + 2H_2O	0.42863	-1450.76136	0.26147	-1450.92851	53.3	40.4
H-4-IM3	0.18359	-610.94202	0.11425	-611.01136		
Glu	0.19958	-686.98102	0.12813	-687.05247		
H-4-IM3 + Glu + 2H_2O	0.42575	-1450.75014	0.23024	-1450.94565	82.7	-4.6
H-4-TS2	0.20970	-687.35906	0.13555	-687.43321		
H-4-TS2 + Glu + H_2O	0.43057	-1450.75364	0.25761	-1450.92659	73.6	45.4
H-4-IM4	0.21272	-687.37017	0.14024	-687.44265		
H-4-IM4 + Glu + H_2O	0.43359	-1450.76474	0.26230	-1450.93603	44.4	20.6
H-4-IM5	0.23721	-763.80694	0.15668	-763.88747		
H-4-IM5 + Glu	0.43679	-1450.78796	0.28481	-1450.93994	-16.6	10.4
2Glu + H_3O^+	0.43226	-1450.77169	0.25962	-1450.94433	26.2	-1.2

Table S15. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the hydrolysis of cellobiulose (CBU) to glucose (Glu) and *β*-D-fructofuranoses (*β*-FF) (CBU + H_2O → Glu + *β*-FF) catalyzed by H_3O^+ at M06-2X/6-311++G(d,p) level in aqueous media under experimental temperature and pressure (493.0 K and 24.3 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
CB2	0.37669	-1297.55845	0.27153	-1297.66360		
H_3O^+	0.03310	-76.80965	0.00337	-76.83939		
H_2O	0.02129	-76.41355	-0.00607	-76.44091		
CB2 + H_3O^+ + H_2O	0.43108	-1450.78165	0.26884	-1450.94389	0.0	0.0
CBU	0.37527	-1297.54943	0.26573	-1297.65897		
CBU + H_3O^+ + H_2O	0.42966	-1450.77263	0.26303	-1450.93926	23.7	12.2
CBUH	0.38793	-1297.93407	0.27763	-1298.04437		
CBUH + 2H_2O	0.43051	-1450.76118	0.26550	-1450.92619	53.7	46.5
CBU-H-TS1	0.38675	-1297.92443	0.27767	-1298.03351		
CBU-H-TS1 + 2H_2O	0.42933	-1450.75154	0.26554	-1450.91532	79.1	75.0
CBUH-IM2	0.38581	-1297.92635	0.27253	-1298.03963		
CBUH-IM2 + 2H_2O	0.42839	-1450.75345	0.26040	-1450.92145	74.0	58.9
H-4-IM3	0.18359	-610.94202	0.11425	-611.01136		
β-FF	0.20012	-686.98019	0.12836	-687.05196		
H-4-IM3 + β-FF + 2H_2O	0.42630	-1450.74931	0.23048	-1450.94513	84.9	-3.3
H-4-TS2	0.20970	-687.35906	0.13555	-687.43321		
H-4-TS2 + β-FF + H_2O	0.43111	-1450.75281	0.25784	-1450.92608	75.7	46.8
H-4-IM4	0.21272	-687.37017	0.14024	-687.44265		
H-4-IM4 + β-FF + H_2O	0.43414	-1450.76391	0.26253	-1450.93552	46.6	22.0
H-4-IM5	0.23721	-763.80694	0.15668	-763.88747		
H-4-IM5 + β-FF	0.43733	-1450.78713	0.28504	-1450.93942	-14.4	11.7
Glu	0.19958	-686.98102	0.12813	-687.05247		
Glu + β-FF + H_3O^+	0.43281	-1450.77086	0.25985	-1450.94381	28.3	0.2

Table S16. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the conversion of *β*-D-glucopyranose (Glu) to 5-hydroxymethylfurfural (HMF) (Glu → HMF + 3H_2O) in the absence of catalyst and H_2O at M06-2X/6-311++G(d,p) level in aqueous media under experimental temperature and pressure (493.0 K and 24.3 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
Glu	0.19958	-686.98102	0.12813	-687.05247	0.0	0.0
H_2O	0.02129	-76.41355	-0.00607	-76.44091		
u-GTS1	0.19391	-686.91038	0.12230	-686.98199	185.5	185.0
chain-Glu	0.19704	-686.96458	0.12192	-687.03971	43.2	33.5
u-GTS2	0.19316	-686.90819	0.11873	-686.98261	191.2	183.4
chain-Fruc	0.19710	-686.97031	0.11982	-687.04759	28.1	12.8
u-GTS3	0.19529	-686.91556	0.12659	-686.98427	171.9	179.1
β-FF	0.20012	-686.98019	0.12836	-687.05196	2.2	1.4
u-FFTS1	0.19166	-686.88756	0.11315	-686.96607	245.4	226.8
u-FFIM2	0.17042	-610.54011	0.10068	-610.60985		
u-FFIM2 + H2O	0.19172	-686.95366	0.09462	-687.05076	71.8	4.5
u-FFTS2	0.16710	-610.49739	0.10501	-610.55949		
u-FFTS2 + H2O	0.18839	-686.91095	0.09894	-687.00040	184.0	136.7
u-FFIM3	0.14140	-534.12894	0.07746	-534.19288		
u-FFIM3 + 2H2O	0.18398	-686.95605	0.06532	-687.07470	65.6	-58.4
u-FFTS3	0.13362	-534.04256	0.06838	-534.10779		
u-FFTS3 + 2H2O	0.17620	-686.86966	0.05625	-686.98961	292.4	165.0
HMF	0.11341	-457.73550	0.05413	-457.79478		
HMF + 3H2O	0.17729	-686.97615	0.03593	-687.11751	12.8	-170.8

Table S17. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the conversion of *β*-D-glucopyranose (Glu) to 5-hydroxymethylfurfural (HMF) (Glu → HMF + 3H_2O) in the presence of explicit H_2O at M06-2X/6-311++G(d,p) level in aqueous media under experimental temperature and pressure (493.0 K and 24.3 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
Glu	0.19958	-686.98102	0.12813	-687.05247		
H_2O	0.02129	-76.41355	-0.00607	-76.44091		
Glu + H_2O	0.22087	-763.39457	0.12206	-763.49338	0.0	0.0
W-GIM1	0.22449	-763.39919	0.14370	-763.47998	-12.1	35.2
W-GTS1	0.21817	-763.36142	0.14082	-763.43877	87.0	143.4
W-GIM2	0.22155	-763.37835	0.13786	-763.46204	42.6	82.3
W-GIM3	0.22147	-763.38292	0.13586	-763.46853	30.6	65.3
W-GTS2	0.21600	-763.33214	0.13370	-763.41444	163.9	207.3
W-GIM4	0.22190	-763.38802	0.13546	-763.47446	17.2	49.7
W-GIM5	0.22297	-763.39094	0.14169	-763.47222	9.5	55.6
W-GTS3	0.21874	-763.35937	0.14454	-763.43356	92.4	157.0
W-GIM6	0.22529	-763.39962	0.14542	-763.47949	-13.2	36.5
W-FFTS1	0.21599	-763.31645	0.13430	-763.39813	205.1	250.1
W-FFIM2	0.19540	-686.96087	0.11863	-687.03763		
W-FFIM2 + H_2O	0.21669	-763.37442	0.11257	-763.47854	52.9	39.0
W-FFTS2	0.19304	-686.92342	0.11934	-686.99712		
W-FFTS2 + H_2O	0.21433	-763.33697	0.11327	-763.43803	151.2	145.3
W-FFIM3	0.16621	-610.54534	0.09210	-610.61945		
W-FFIM3 + 2H_2O	0.20879	-763.37244	0.07997	-763.50126	58.1	-20.7
W-FFTS3	0.15648	-610.47866	0.07811	-610.55703		
W-FFTS3 + 2H_2O	0.19906	-763.30576	0.06598	-763.43884	233.2	143.2
HMF	0.11341	-457.73550	0.05413	-457.79478		
HMF + 4H_2O	0.19858	-763.38970	0.02986	-763.55841	12.8	-170.8

Table S18. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the conversion of *β*-D-glucopyranose (Glu) to 5-hydroxymethylfurfural (HMF) (Glu → HMF + 3H_2O) catalyzed by H_3O^+ at M06-2X/6-311++G(d,p) level in aqueous media under experimental temperature and pressure (493.0 K and 24.3 atm).

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
Glu	0.19958	-686.98102	0.12813	-687.05247		
H_3O^+	0.03310	-76.80965	0.00337	-76.83939		
H2O	0.02129	-76.41355	-0.00607	-76.44091		
Glu + H3O	0.23268	-763.79067	0.13149	-763.89186	0.0	0.0
H-5-IM1	0.23665	-763.81091	0.15657	-763.89100	-53.1	2.3
H-5-IM2	0.21252	-687.37610	0.14059	-687.44802		
H-5-IM2 + H_2O	0.23381	-763.78965	0.13452	-763.88893	2.7	7.7
H-5-TS1	0.23098	-763.79165	0.14837	-763.87426	-2.6	46.2
H-5-IM3	0.23356	-763.79280	0.14817	-763.87818	-5.6	35.9
H-5-TS2a	0.23042	-763.76359	0.14468	-763.84933	71.1	111.7
H-5-IM4	0.20891	-687.36126	0.13381	-687.43636		
H-5-IM4 + H_2O	0.23020	-763.77482	0.12775	-763.87727	41.6	38.3
H-5-TS2	0.20544	-687.34591	0.13309	-687.41825		
H-5-TS2 + H_2O	0.22673	-763.75946	0.12703	-763.85916	81.9	85.9
H-5-IM5	0.20891	-687.37278	0.13376	-687.44793		
H-5-IM5 + H_2O	0.23020	-763.78633	0.12770	-763.88883	11.4	7.9
H-5-IM6	0.21184	-687.37061	0.13757	-687.44489		
H-5-IM6 + H_2O	0.23314	-763.78417	0.13150	-763.88580	17.1	15.9
H-5-TS3	0.23552	-763.79135	0.15428	-763.87258	-1.8	50.6
H-5-IM7	0.23923	-763.80810	0.16275	-763.88458	-45.8	19.1
β-FF	0.20012	-686.98019	0.12836	-687.05196		
β-FF + H_2O	0.23323	-763.78984	0.13173	-763.89134	2.2	1.4
H-GIM8	0.21140	-687.37690	0.13781	-687.45049		
H-GIM8 + H_2O	0.23269	-763.79045	0.13174	-763.89139	0.6	1.2
H-FFTS1	0.20858	-687.37165	0.13396	-687.44628		
H-FFTS1 + H_2O	0.22987	-763.78521	0.12789	-763.88719	14.3	12.3
H-FFIM1	0.18297	-610.95316	0.11232	-611.02381		
H-FFIM1 + 2H_2O	0.22555	-763.78026	0.10019	-763.90562	27.3	-36.1
H-FFIM2	0.18448	-610.94947	0.11607	-611.01788		
H-FFIM2 + 2H_2O	0.22706	-763.77657	0.10394	-763.89969	37.0	-20.6
H-FFTS2	0.17971	-610.92175	0.11080	-610.99066		
H-FFTS2 + 2H_2O	0.22229	-763.74885	0.09866	-763.87248	109.8	50.9

H-FFIM3	0.18416	-610.94011	0.11533	-611.00894		

Continued from **Table S18**

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
H-FFIM3 + $2H_2O$	0.22674	-763.76721	0.10319	-763.89076	61.6	2.9
H-FFTS3	0.18026	-610.93802	0.11502	-611.00327		
H-FFTS3 + $2H_2O$	0.22285	-763.76512	0.10288	-763.88508	67.1	17.8
H-FFIM4	0.18492	-610.93993	0.11684	-611.00801		
H-FFIM4 + $2H_2O$	0.22750	-763.76703	0.10470	-763.88983	62.1	5.3
H-FFTS4	0.17279	-610.88710	0.09524	-610.96465		
H-FFTS4 + $2H_2O$	0.21537	-763.71421	0.08311	-763.84646	200.8	119.2
H-FFIM5	0.15430	-534.52757	0.08908	-534.59279		
H-FFIM5 + $3H_2O$	0.21818	-763.76822	0.07088	-763.91552	58.9	-62.1
H-FFTS5	0.14980	-534.46720	0.08793	-534.52907		
H-FFTS5 + $3H_2O$	0.21367	-763.70786	0.06973	-763.85180	217.4	105.2
H-6b-IM6	0.15517	-534.51992	0.09094	-534.58415		
H-6b-IM6 + $3H_2O$	0.21905	-763.76057	0.07274	-763.90687	79.0	-39.4
H-FFIM7	0.17954	-610.95377	0.10744	-611.02587		
H-FFIM7 + $2H_2O$	0.22555	-763.78026	0.10019	-763.90562	27.3	-36.1
H-FFTS6	0.17461	-610.93162	0.10286	-611.00337		
H-FFTS6 + $2H_2O$	0.21719	-763.75873	0.09073	-763.88519	83.9	17.5
u-FFIM3	0.14140	-534.12894	0.07746	-534.19288		
u-FFIM3 + $2H_2O$ + H_3O^+	0.21708	-763.76570	0.06869	-763.91409	65.6	-58.4
H-FFTS7	0.14853	-534.47686	0.08503	-534.54035		
H-FFTS7 + $3H_2O$	0.21240	-763.71751	0.06684	-763.86307	192.1	75.6
H-FFIM8	0.15507	-534.52640	0.09092	-534.59055		
H-FFIM8 + $3H_2O$	0.21895	-763.76706	0.07272	-763.91328	62.0	-56.2
H-FFTS8	0.15142	-534.51777	0.08571	-534.58348		
H-FFTS8 + $3H_2O$	0.21529	-763.75843	0.06751	-763.90621	84.7	-37.7
HMFH-IM1	0.15035	-534.52752	0.07931	-534.59857		
HMFH-IM1 + $3H_2O$	0.21422	-763.76818	0.06111	-763.92129	59.0	-77.3
HMFH-TS1	0.14624	-534.51895	0.07842	-534.58677		
HMFH-TS1 + $3H_2O$	0.21011	-763.75961	0.06022	-763.90949	81.6	-46.3
HMF	0.11341	-457.73550	0.05413	-457.79478		
HMF + H_3O^+ + $3H_2O$	0.21039	-763.78580	0.03930	-763.95689	12.8	-170.7
H-6b-IM1	0.23943	-763.80998	0.16363	-763.88578	-50.7	16.0
H-6b-TS1	0.23361	-763.78990	0.15179	-763.87173	2.0	52.9
H-6b-IM2	0.20857	-687.36815	0.13093	-687.44579		
H-6b-IM2 + H_2O	0.22986	-763.78171	0.12487	-763.88670	23.5	13.6
H-6b-TS2	0.20345	-687.35317	0.12999	-687.42663		
H-6b-TS2 + H_2O	0.22474	-763.76672	0.12392	-763.86754	62.9	63.9

H-6b-IM3	0.20702	-687.37094	0.12940	-687.44856		

Continued from **Table S18**

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
H-6b-IM3 + H_2O	0.22831	-763.78449	0.12334	-763.88947	16.2	6.3
H-6b-TS3	0.20422	-687.34464	0.12440	-687.42446		
H-6b-TS3 + H_2O	0.22551	-763.75820	0.11834	-763.86536	85.3	69.6
6-H-TS2	0.17724	-610.88661	0.10551	-610.95834		
6-H-TS2 + $2H_2O$	0.21982	-763.71372	0.09338	-763.84016	202.0	135.7
6-H-IM3	0.15049	-534.47901	0.08460	-534.54489		
6-H-IM3 + $3H_2O$	0.21436	-763.71967	0.06641	-763.86762	186.4	63.6
8-H-TS1	0.15038	-534.47667	0.08680	-534.54025		
8-H-TS1 + $3H_2O$	0.21425	-763.71733	0.06861	-763.86297	192.6	75.8
8-H-IM2	0.15393	-534.53953	0.08922	-534.60424		
8-H-IM2 + $3H_2O$	0.21780	-763.78019	0.07102	-763.92697	27.5	-92.2
8-H-TS2	0.14833	-534.47981	0.08457	-534.54358		
8-H-TS2 + 3H2O	0.21221	-763.72047	0.06637	-763.86631	184.3	67.1
8-H-IM3	0.12495	-458.12357	0.06447	-458.18405		
8-H-IM3 + $4H_2O$	0.21011	-763.77778	0.04021	-763.94768	33.8	-146.6
8-H-IM4	0.14925	-534.53905	0.07729	-534.61102		
8-H-IM4 + $3H_2O$	0.21312	-763.77971	0.05909	-763.93374	28.8	-110.0
8-H-TS3	0.14523	-534.53035	0.07630	-534.59927		
8-H-TS3 + $3H_2O$	0.20910	-763.77100	0.05811	-763.92200	51.6	-79.1
HMF	0.11341	-457.73550	0.05413	-457.79478		
HMF + H_3O^+ + $3H_2O$	0.21039	-763.78580	0.03930	-763.95689	12.8	-170.7

Table S19. Zero-point energies (*ZPE*, hartree), thermal correction to enthalpy (H_0, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal enthalpies (H_c, hartree) with *ZPE* and thermal corrections, and sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, entropies (S, cal mol^{-1} K^{-1}), and relative energies (E_r, kJ mol^{-1}), relative enthalpies (H_r, kJ mol^{-1}), relative Gibbs free energies (G_r, kJ mol^{-1}) and relative entropies (S_r, J mol^{-1} K^{-1}) of various species with respect to the reactants for the conversion of *β*-cellobiose into both glucose and HMF (CB → Glu + HMF + 2H_2O) in the presence of H_3O^+ alone and in the presence of H_3O^+ together with the counterpart anion (A^- = Cl^-, Br^-, NO_3^-, HCO_3^-, FA^-, LA^-, and $FDCA^-$) at M06-2X/6-311++G(d,p) level in aqueous media under experimental temperature and pressure.

Species	*ZPE*	E_c	H_0	H_c	G_0	G_c	S	E_r	H_r	G_r	S_r
CB2	0.37669	-1297.55845	0.43646	-1297.49867	0.27153	-1297.66360	209.928				
H_3O^+	0.03310	-76.80965	0.03950	-76.80326	0.00337	-76.83939	45.988				
H_2O	0.02129	-76.41355	0.02761	-76.40723	-0.00607	-76.44091	42.864				
CB2 + H_3O^+	0.40979	-1374.36810	0.47596	-1374.30192	0.27490	-1374.50298	255.916	0.0	0.0	0.0	0.0
H-IM1	0.41396	-1374.38778	0.47987	-1374.32187	0.30082	-1374.50092	227.895	-51.7	-52.4	5.4	-117.3
H-TS2	0.38231	-1297.91890	0.44337	-1297.85785	0.27505	-1298.02616	214.236				
H-TS2 + H_2O	0.40361	-1374.33245	0.47098	-1374.26508	0.26899	-1374.46707	257.100	93.6	96.7	94.3	5.0
H-IM15 (protonated glycosyl-HMF)	0.32881	-1145.10883	0.38166	-1145.05598	0.23063	-1145.20701	192.239				
H-IM15 + 3H_2O	0.39269	-1374.34948	0.46449	-1374.27768	0.21243	-1374.52974	320.831	48.9		-70.2	271.7
Cl^-	0.00000	-460.37264	0.00390	-460.36873	-0.02182	-460.39446	32.744				
CB2 + H_3O^+ + Cl^-	0.40979	-1834.74073	0.47986	-1834.67066	0.25308	-1834.89744	288.660	0.0	0.0	0.0	0.0
H-IM1-Cl	0.41342	-1834.77739	0.48187	-1834.70894	0.29354	-1834.89726	239.707	-96.2	-100.5	0.5	-204.9
H-TS2-Cl	0.38257	-1758.30834	0.44739	-1758.24352	0.26634	-1758.42457	230.444				
H-TS2-Cl + H_2O	0.40386	-1834.72189	0.47500	-1834.65075	0.26027	-1834.86548	273.308	49.5	52.3	83.9	-64.3
H-IM15-Cl	0.32952	-1605.49785	0.38585	-1605.44152	0.22264	-1605.60473	207.736				
H-IM15-Cl + 3H_2O	0.39339	-1834.73851	0.46868	-1834.66322	0.20444	-1834.92745	336.328	5.8	19.5	-78.8	199.5

Continued from **Table S19**

Species	*ZPE*	E_c	H_0	H_c	G_0	G_c	S	E_r	H_r	G_r	S_r
Br^-	0.00000	-2574.34124	0.00390	-2574.33734	-0.02373	-2574.36497	35.171				
CB2 + H_3O^+ + Br^-	0.40979	-3948.70934	0.47986	-3948.63926	0.25117	-3948.86795	291.087	0.0	0.0	0.0	0.0
H-IM1-Br	0.41400	-3948.75025	0.48222	-3948.68203	0.29314	-3948.87111	240.668	-107.4	-112.3	-8.3	-211.1
H-TS2-Br	0.38326	-3872.28142	0.44759	-3872.21709	0.26681	-3872.39787	230.113				
H-TS2-Br + H_2O	0.40455	-3948.69497	0.47520	-3948.62432	0.26074	-3948.83878	272.977	37.7	39.2	76.6	-75.8
H-IM15-Br	0.32951	-3719.47107	0.38570	-3719.41489	0.22307	-3719.57752	207.003				
H-IM15-Br + $3H_2O$	0.39339	-3948.71173	0.46853	-3948.63658	0.20487	-3948.90024	335.595	-6.3	7.0	-84.8	186.3
NO_3^-	0.01427	-280.42900	0.02216	-280.42112	-0.02647	-280.46637	61.890				
CB2 + H_3O^+ + NO_3^-	0.42406	-1654.79710	0.49812	-1654.72304	0.24843	-1654.96936	317.806	0.0	0.0	0.0	0.0
H-IM1-NO3	0.43002	-1654.82856	0.50378	-1654.75479	0.30233	-1654.95624	256.413	-82.6	-83.4	34.4	-257.0
H-TS2-NO3	0.39813	-1578.36057	0.46866	-1578.29004	0.27320	-1578.48550	248.793				
H-TS2-NO3 + H_2O	0.41942	-1654.77413	0.49627	-1654.69727	0.26713	-1654.92641	291.657	60.3	67.7	112.8	-109.5
H-IM15-NO3	0.34592	-1425.54911	0.40758	-1425.48745	0.23291	-1425.66212	222.322				
H-IM15-NO3 + $3H_2O$	0.40980	-1654.78976	0.49041	-1654.70915	0.21472	-1654.98484	350.914	19.3	36.5	-40.6	138.6
HCO_3^-	0.02656	-264.53854	0.03556	-264.52955	-0.01507	-264.58017	64.439				
CB2 + H_3O^+ + HCO_3^-	0.43635	-1638.90663	0.51152	-1638.83147	0.25983	-1639.08316	320.355	0.0	0.0	0.0	0.0
H-IM1-HCO3	0.44182	-1638.94245	0.51659	-1638.86767	0.31310	-1639.07116	259.010	-94.0	-95.0	31.5	-256.8
H-TS2-HCO3	0.40964	-1562.47421	0.48108	-1562.40278	0.28235	-1562.60150	252.944				
H-TS2-HCO3 + H_2O	0.43093	-1638.88776	0.50869	-1638.81001	0.27629	-1639.04241	295.808	49.5	56.3	107.0	-102.8
H-IM15-HCO3	0.35712	-1409.66305	0.41989	-1409.60028	0.24168	-1409.77849	226.830				

Continued from **Table S19**

Species	*ZPE*	E_c	H_0	H_c	G_0	G_c	*S*	E_r	H_r	G_r	S_r
H-IM15-HCO3 + $3H_2O$	0.42100	-1638.90370	0.50272	-1638.82198	0.22348	-1639.10122	355.422	7.7	24.9	-47.4	146.8
FA^-	0.02098	-189.28514	0.02815	-189.27798	-0.01681	-189.32293	57.217				
CB2 + H_3O^+ + FA^-	0.43077	-1563.65323	0.50411	-1563.57990	0.25810	-1563.82591	313.133	0.0	0.0	0.0	0.0
H-IM1-FA	0.43597	-1563.68752	0.50882	-1563.61467	0.30872	-1563.81478	254.697	-90.0	-91.3	29.2	-244.6
H-TS2-FA	0.40449	-1487.22138	0.47369	-1487.15217	0.28166	-1487.34420	244.425				
H-TS2-FA + H_2O	0.42578	-1563.63493	0.50130	-1563.55940	0.27560	-1563.78511	287.289	48.1	53.8	107.1	-108.2
H-IM15-FA	0.35148	-1334.41026	0.41219	-1334.34955	0.23937	-1334.52237	219.969				
H-IM15-FA + $3H_2O$	0.41535	-1563.65092	0.49502	-1563.57124	0.22117	-1563.84509	348.561	6.1	22.7	-50.4	148.3
LA^-	0.11503	-420.44155	0.13674	-420.41984	0.04999	-420.50660	110.422				
CB2 + H_3O^+ + LA^-	0.52482	-1794.80965	0.61270	-1794.72177	0.32489	-1795.00958	366.338	0.0	0.0	0.0	0.0
H-IM1-LA	0.52958	-1794.84717	0.61721	-1794.75954	0.37963	-1794.99712	302.395	-98.5	-99.2	32.7	-267.7
H-TS2-LA	0.49956	-1718.37795	0.58311	-1718.29439	0.35657	-1718.52094	288.356				
H-TS2-LA + H_2O	0.52085	-1794.79150	0.61072	-1794.70163	0.35050	-1794.96185	331.220	47.7	52.9	125.3	-147.0
H-IM15-LA	0.44669	-1565.56704	0.52143	-1565.49230	0.31547	-1565.69827	262.158				
H-IM15-LA + $3H_2O$	0.51056	-1794.80770	0.60426	-1794.71400	0.29727	-1795.02099	390.750	5.1	20.4	-30.0	102.2
$FDCA^-$	0.08730	-606.61832	0.11014	-606.59547	0.02345	-606.68217	110.350				
CB2 + H_3O^+ + $FDCA^-$	0.49709	-1980.98641	0.58610	-1980.89740	0.29835	-1981.18515	366.266	0.0	0.0	0.0	0.0
H-IM1-FDCA	0.50209	-1981.02186	0.59088	-1980.93307	0.35181	-1981.17214	304.302	-93.1	-93.6	34.2	-259.4
H-TS2-FDCA	0.47138	-1904.55344	0.55650	-1904.46832	0.32586	-1904.69896	293.571				

Continued from **Table S19**

Species	*ZPE*	E_c	H_0	H_c	G_0	G_c	*S*	E_r	H_r	G_r	S_r
H-TS2-FDCA + H_2O	0.49267	-1980.96699	0.58411	-1980.87555	0.31979	-1981.13987	336.435	51.0	57.4	118.9	-124.9
H-IM15-FDCA	0.41761	-1751.74290	0.49442	-1751.66608	0.28070	-1751.87981	272.034				
H-IM15-FDCA + $3H_2O$	0.48148	-1980.98356	0.57725	-1980.88778	0.26250	-1981.20253	400.626	7.5	25.3	-45.6	143.8

Table S20. Zero-point energies (*ZPE*, hartree), thermal correction to enthalpy (H_0, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal enthalpies (H_c, hartree) with *ZPE* and thermal corrections, and sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, entropies (S, cal mol^{-1} K^{-1}), and relative energies (E_r, kJ mol^{-1}), relative enthalpies (H_r, kJ mol^{-1}), relative Gibbs free energies (G_r, kJ mol^{-1}) and relative entropies (S_r, J mol^{-1} K^{-1}) of various species with respect to the reactants for the hydrolysis of *β*-cellobiose (CB) to glucose (Glu) (CB + H_2O → 2Glu) in the presence of H_3O^+ alone and in the presence of H_3O^+ together with the counterpart anion (A^- = Cl^-, Br^-, NO_3^-, HCO_3^-, FA^-, LA^-, and $FDCA^-$) at M06-2X/6-311++G(d,p) level in aqueous media under experimental temperature and pressure.

Species	*ZPE*	E_c	H_0	H_c	G_0	G_c	S	E_r	H_r	G_r	S_r
CB2	0.37669	-1297.55845	0.43646	-1297.49867	0.27153	-1297.66360	209.928				
H_3O^+	0.03310	-76.80965	0.03950	-76.80326	0.00337	-76.83939	45.988				
H_2O	0.02129	-76.41355	0.02761	-76.40723	-0.00607	-76.44091	42.864				
CB2 + H_3O^+	0.40979	-1374.36810	0.47596	-1374.30192	0.27490	-1374.50298	255.916	0.0	0.0	0.0	0.0
H-4-IM1	0.38975	-1297.94325	0.45063	-1297.88237	0.28341	-1298.04959	212.845				
H-4-IM1 + 2H_2O	0.41104	-1374.35680	0.47824	-1374.28960	0.27734	-1374.49050	255.709	29.7	32.3	32.8	-0.9
H-4-TS1	0.38717	-1297.93196	0.44843	-1297.87070	0.27924	-1298.03990	215.355				
H-4-TS1 + H_2O	0.40846	-1374.34552	0.47604	-1374.27793	0.27317	-1374.48080	258.219	59.3	63.0	58.2	9.6
Cl^-	0.00000	-460.37264	0.00390	-460.36873	-0.02182	-460.39446	32.744				
CB2 + H_3O^+ + Cl^-	0.40979	-1834.74073	0.47986	-1834.67066	0.25308	-1834.89744	288.660	0.0	0.0	0.0	0.0
H-4-IM1-Cl	0.39234	-1758.33156	0.45591	-1758.26799	0.28009	-1758.44381	223.795				
H-4-IM1-Cl + H_2O	0.41363	-1834.74511	0.48352	-1834.67522	0.27402	-1834.88472	266.659	-11.5	-12.0	33.4	-92.1
H-4-TS1-Cl	0.38818	-1758.32314	0.45255	-1758.25878	0.27357	-1758.43775	227.806				
H-4-TS1-Cl + H_2O	0.40947	-1834.73669	0.48016	-1834.66601	0.26751	-1834.87866	270.670	10.6	12.2	49.3	-75.3
Br^-	0.00000	-2574.34124	0.00390	-2574.33734	-0.02373	-2574.36497	35.171				

Continued from **Table S20**

Species	*ZPE*	E_c	H_0	H_c	G_0	G_c	S	E_r	H_r	G_r	S_r
CB2 + H_3O^+ + Br^-	0.40979	-3948.70934	0.47986	-3948.63926	0.25117	-3948.86795	291.087	0.0	0.0	0.0	0.0
H-4-IM1-Br	0.39105	-3872.30593	0.45525	-3872.24173	0.27618	-3872.42080	227.927				
H-4-IM1-Br + H_2O	0.41234	-3948.71948	0.48286	-3948.64896	0.27011	-3948.86171	270.791	-26.6	-25.5	16.4	-85.0
H-4-TS1-Br	0.38798	-3872.29699	0.45250	-3872.23248	0.27147	-3872.41351	230.419				
H-4-TS1-Br + H_2O	0.40928	-3948.71055	0.48011	-3948.63971	0.26540	-3948.85442	273.283	-3.2	-1.2	35.5	-74.5
NO_3^-	0.01427	-280.42900	0.02216	-280.42112	-0.02647	-280.46637	61.890				
CB2 + H_3O^+ + NO_3^-	0.42406	-1654.79710	0.49812	-1654.72304	0.24843	-1654.96936	317.806	0.0	0.0	0.0	0.0
H-4-IM1-NO3	0.40680	-1578.38452	0.47676	-1578.31455	0.28457	-1578.50674	260.609				
H-4-IM1-NO3 + H_2O	0.42809	-1654.79807	0.50437	-1654.72178	0.27850	-1654.94765	303.473	-2.5	3.3	57.0	-60.0
H-4-TS1-NO3	0.40426	-1578.37573	0.47435	-1578.30564	0.28129	-1578.49870	245.738				
H-4-TS1-NO3 + H_2O	0.42555	-1654.78928	0.50196	-1654.71287	0.27522	-1654.93961	288.602	20.5	26.7	78.1	-122.2
HCO_3^-	0.02656	-264.53854	0.03556	-264.52955	-0.01507	-264.58017	64.439				
CB2 + H_3O^+ + HCO_3^-	0.43635	-1638.90663	0.51152	-1638.83147	0.25983	-1639.08316	320.355	0.0	0.0	0.0	0.0
H-4-IM1-HCO3	0.41807	-1562.49856	0.48899	-1562.42765	0.29463	-1562.62201	247.385				
H-4-IM1-HCO3 + H_2O	0.43936	-1638.91212	0.51660	-1638.83488	0.28856	-1639.06292	290.249	-14.4	-9.0	53.2	-126.0
H-4-TS1-HCO3	0.41486	-1562.49064	0.48622	-1562.41928	0.28874	-1562.61676	251.356				
H-4-TS1-HCO3 + H_2O	0.43616	-1638.90419	0.51383	-1638.82651	0.28268	-1639.05767	294.220	6.4	13.0	66.9	-109.4
FA^-	0.02098	-189.28514	0.02815	-189.27798	-0.01681	-189.32293	57.217				
CB2 + H_3O^+ + FA^-	0.43077	-1563.65323	0.50411	-1563.57990	0.25810	-1563.82591	313.133	0.0	0.0	0.0	0.0

Continued from **Table S20**

Species	*ZPE*	E_c	H_0	H_c	G_0	G_c	*S*	E_r	H_r	G_r	S_r
H-4-IM1-FA	0.41445	-1487.24406	0.48239	-1487.17611	0.29726	-1487.36124	235.642				
H-4-IM1-FA + H_2O	0.43574	-1563.65761	0.51000	-1563.58334	0.29120	-1563.80215	278.506	-11.5	-9.0	62.4	-144.9
H-4-TS1-FA	0.41022	-1487.23710	0.47886	-1487.16846	0.28882	-1487.35850	241.894				
H-4-TS1-FA + H_2O	0.43151	-1563.65065	0.50647	-1563.57569	0.28275	-1563.79941	284.758	6.8	11.1	69.6	-118.8
LA^-	0.11503	-420.44155	0.13674	-420.41984	0.04999	-420.50660	110.422				
CB2 + H_3O^+ + LA^-	0.52482	-1794.80965	0.61270	-1794.72177	0.32489	-1795.00958	366.338	0.0	0.0	0.0	0.0
H-4-IM1-LA	0.50683	-1718.40303	0.58995	-1718.31990	0.36457	-1718.54528	286.873				
H-4-IM1-LA + H_2O	0.52812	-1794.81658	0.61756	-1794.72714	0.35851	-1794.98619	329.737	-18.2	-14.1	61.4	-153.2
H-4-TS1-LA	0.50426	-1718.39497	0.58760	-1718.31163	0.36123	-1718.53801	288.142				
H-4-TS1-LA + H_2O	0.52555	-1794.80853	0.61521	-1794.71886	0.35516	-1794.97892	331.006	3.0	7.6	80.5	-147.9
$FDCA^-$	0.08730	-606.61832	0.11014	-606.59547	0.02345	-606.68217	110.350				
CB2 + H_3O^+ + $FDCA^-$	0.49709	-1980.98641	0.58610	-1980.89740	0.29835	-1981.18515	366.266	0.0	0.0	0.0	0.0
H-4-IM1-FDCA	0.47902	-1904.57799	0.56381	-1904.49320	0.33528	-1904.72173	290.871				
H-4-IM1-FDCA + H_2O	0.50031	-1980.99154	0.59142	-1980.90044	0.32922	-1981.16263	290.871	-13.5	-8.0	59.1	-315.6
H-4-TS1-FDCA	0.47628	-1904.56993	0.56122	-1904.48498	0.33238	-1904.71382	291.277				
H-4-TS1-FDCA + H_2O	0.49757	-1980.98348	0.58883	-1980.89222	0.32632	-1981.15473	334.141	7.7	13.6	79.9	-134.5

Table S21. Zero-point energies (*ZPE*, hartree), thermal correction to enthalpy (H_0, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, Sum of electronic and thermal enthalpies (H_c, hartree) with *ZPE* and thermal corrections, and Sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, entropies (S, cal mol^{-1} K^{-1}), and relative energies (E_r, kJ mol^{-1}), relative enthalpies (H_r, kJ mol^{-1}), relative Gibbs free energies (G_r, kJ mol^{-1}) and relative entropies (S_r, J mol^{-1} K^{-1}) of various species with respect to the reactants for the conversion of *β*-D-glucopyranose (Glu) to 5-hydroxymethylfurfural (HMF) (Glu → HMF + 3H_2O) in the presence of H_3O^+ alone and in the presence of H_3O^+ together with the counterpart anion (A^- = Cl^-, Br^-, NO_3^-, HCO_3^-, FA^-, LA^-, and $FDCA^-$) at M06-2X/6-311++G(d,p) level in aqueous media under experimental temperature and pressure.

Species	*ZPE*	E_c	H_0	H_c	G_0	G_c	S	E_r	H_r	G_r	S_r
Glu	0.19958	-686.98102	0.23219	-686.94841	0.12813	-687.05247	132.459				
H_3O^+	0.03310	-76.80965	0.03950	-76.80326	0.00337	-76.83939	45.988				
H_2O	0.02129	-76.41355	0.02761	-76.40723	-0.00607	-76.44091	42.864				
Glu + H_3O^+	0.23268	-763.79067	0.27169	-763.75166	0.13149	-763.89186	178.447	0.0	0.0	0.0	0.0
H-5-IM1	0.23665	-763.81091	0.27536	-763.77220	0.15657	-763.89100	151.204	-53.1	-53.9	2.3	-114.0
H-5-TS2	0.20544	-687.34591	0.23803	-687.31332	0.13309	-687.41825	133.570				
H-5-TS2 + H_2O	0.22673	-763.75946	0.26564	-763.72055	0.12703	-763.85916	176.434	81.9	81.7	85.9	-8.4
Cl^-	0.00000	-460.37264	0.00390	-460.36873	-0.02182	-460.39446	32.744				
Glu + H_3O^+ + Cl^-	0.23268	-1224.16331	0.27559	-1224.12040	0.10967	-1224.28632	211.191	0.0	0.0	0.0	0.0
H-5-IM1-Cl	0.23778	-1224.19810	0.27957	-1224.15631	0.15078	-1224.28510	163.925	-91.3	-94.3	3.2	-197.9
H-5-TS2-Cl	0.20648	-1147.73718	0.24350	-1147.70016	0.12511	-1147.81855	150.700				
H-5-TS2-Cl + H_2O	0.22777	-1224.15073	0.27111	-1224.10739	0.11904	-1224.25946	193.564	33.0	34.2	70.5	-73.8
Br^-	0.00000	-2574.34124	0.00390	-2574.33734	-0.02373	-2574.36497	35.171				
Glu + H_3O^+ + Br^-	0.23268	-3338.13191	0.27559	-3338.08900	0.10776	-3338.25683	213.618	0.0	0.0	0.0	0.0

Continued from **Table S21**

Species	*ZPE*	E_c	H_0	H_c	G_0	G_c	S	E_r	H_r	G_r	S_r
H-5-IM1-Br	0.23763	-3338.17125	0.27948	-3338.12940	0.14884	-3338.26004	166.290	-103.3	-106.1	-8.4	-198.1
H-5-TS2-Br	0.20624	-3261.71097	0.24336	-3261.67385	0.12251	-3261.79471	153.828				
H-5-TS2-Br + H_2O	0.22753	-3338.12453	0.27097	-3338.08109	0.11644	-3338.23562	196.692	19.4	20.8	55.7	-70.9
NO_3^-	0.01427	-280.42900	0.02216	-280.42112	-0.02647	-280.46637	61.890				
Glu + H_3O^+ + NO_3^-	0.24695	-1044.21967	0.29384	-1044.17278	0.10503	-1044.36160	240.337	0.0	0.0	0.0	0.0
H-5-IM1-NO3	0.25349	-1044.25263	0.30079	-1044.20533	0.15717	-1044.34895	182.812	-86.5	-85.5	33.2	-240.8
H-5-TS2-NO3	0.22272	-967.78898	0.26530	-967.74640	0.13108	-967.88063	170.843				
H-5-TS2-NO3 + H_2O	0.24402	-1044.20253	0.29291	-1044.15364	0.12501	-1044.32153	213.707	45.0	50.3	105.2	-111.5
HCO_3^-	0.02656	-264.53854	0.03556	-264.52955	-0.01507	-264.58017	64.439				
Glu + H_3O^+ + HCO_3^-	0.25925	-1028.32921	0.30725	-1028.28121	0.11642	-1028.47203	242.886	0.0	0.0	0.0	0.0
H-5-IM1-HCO3	0.26582	-1028.36580	0.31381	-1028.31782	0.17037	-1028.46126	182.576	-96.1	-96.1	28.3	-252.5
H-5-TS2-HCO3	0.23400	-951.90370	0.27759	-951.86010	0.14244	-951.99526	172.032				
H-5-TS2-HCO3 + H_2O	0.25529	-1028.31725	0.30520	-1028.26734	0.13637	-1028.43617	214.896	31.4	36.4	94.2	-117.2
FA^-	0.02098	-189.28514	0.02815	-189.27798	-0.01681	-189.32293	57.217				
Glu + H_3O^+ + FA^-	0.25366	-953.07581	0.29983	-953.02964	0.11469	-953.21479	235.664	0.0	0.0	0.0	0.0
H-5-IM1-FA	0.26048	-953.11259	0.30631	-953.06677	0.16851	-953.20457	175.396	-96.6	-97.5	26.8	-252.3
H-5-TS2-FA	0.22881	-876.65074	0.27015	-876.60940	0.14116	-876.73839	164.184				
H-5-TS2-FA + H_2O	0.25010	-953.06430	0.29776	-953.01664	0.13509	-953.17930	207.048	30.2	34.1	93.2	-119.8

Continued from **Table S21**

Species	*ZPE*	E_c	H_0	H_c	G_0	G_c	S	E_r	H_r	G_r	S_r
LA^-	0.11503	-420.44155	0.13674	-420.41984	0.04999	-420.50660	110.422				
Glu + H_3O^+ + LA^-	0.34771	-1184.23222	0.40843	-1184.17151	0.18148	-1184.39845	288.869	0.0	0.0	0.0	0.0
H-5-IM1-LA	0.35382	-1184.27095	0.41463	-1184.21014	0.23713	-1184.38763	225.925	-101.7	-101.4	28.4	-263.5
H-5-TS2-LA	0.32283	-1107.80848	0.37875	-1107.75256	0.21184	-1107.91947	212.445				
H-5-TS2-LA + H_2O	0.34412	-1184.22203	0.40636	-1184.15979	0.20578	-1184.36037	255.309	26.8	30.8	100.0	-140.5
$FDCA^-$	0.08730	-606.61832	0.11014	-606.59547	0.02345	-606.68217	110.350				
Glu + H_3O^+ + $FDCA^-$	0.31998	-1370.40899	0.38183	-1370.34714	0.15494	-1370.57403	288.797	0.0	0.0	0.0	0.0
H-5-IM1-FDCA	0.32641	-1370.44556	0.38855	-1370.38343	0.20888	-1370.56310	228.690	-96.0	-95.3	28.7	-251.6
H-5-TS2-FDCA	0.29406	-1293.98379	0.35195	-1293.92590	0.17895	-1294.09890	220.212				
H-5-TS2-FDCA + H_2O	0.31535	-1370.39734	0.37956	-1370.33313	0.17288	-1370.53981	263.076	30.6	36.8	89.8	-107.7