Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Effect of Wells-Dawson phosphomolybdic heteropolyacid on conversion of glucose into glycolic acid

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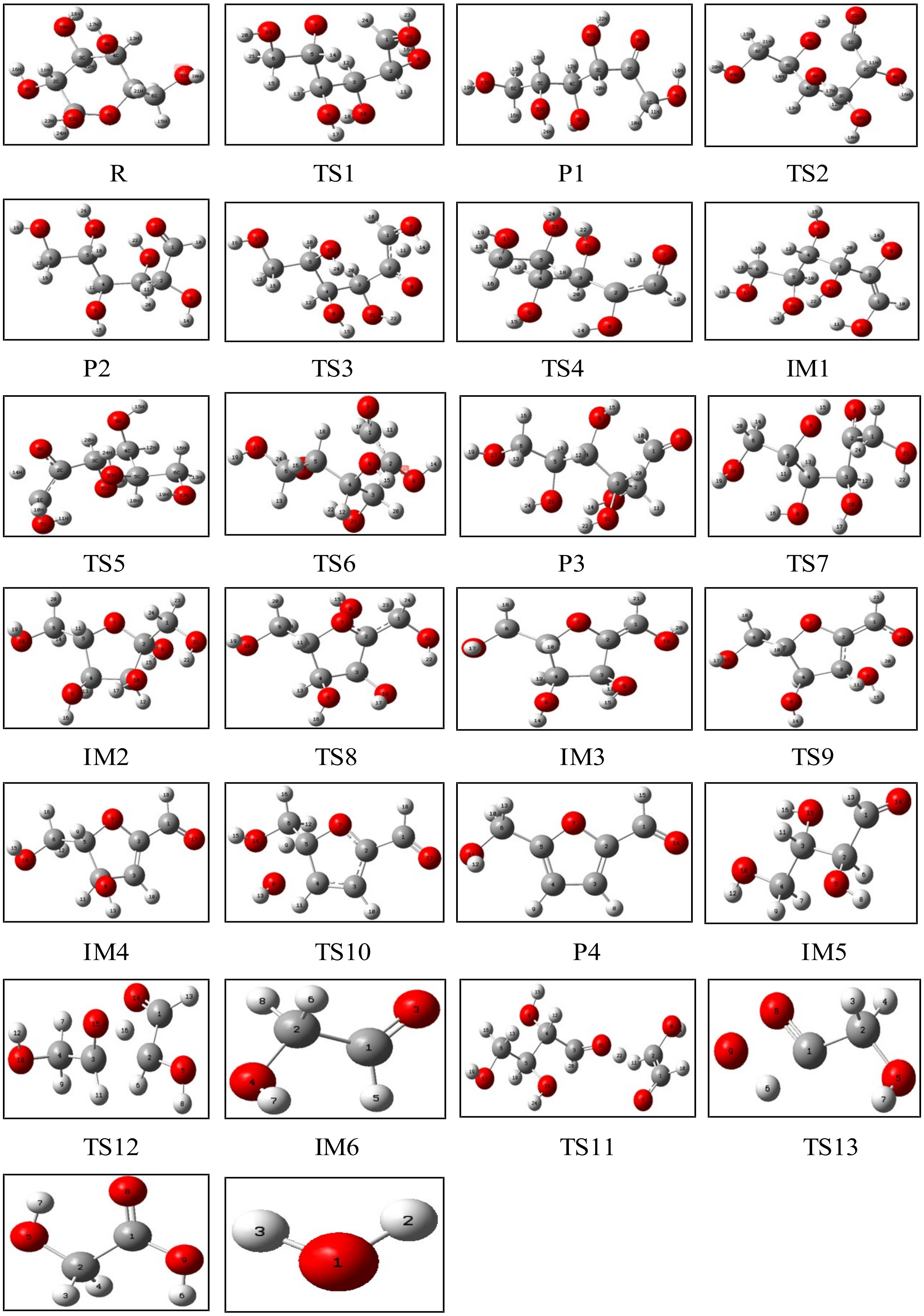
Table S1. Vibration frequency of species at B3LYP/6-31+G(d) level (cm^{-1}).

Species	Frequency	Species	Frequency
R	44.74	IM_1	59.67
IM2	30.75	IM3	33.61
IM4	55.60	IM5	58.64
IM6	66.45	P1	27.92
P2	32.48	P3	36.78
P4	55.81	P5	95
TS1	-339.08	TS2	-1587.01
TS3	-731.98	TS4	-2227.41
TS5	-2275.14	TS6	-2156.24
TS7	-1689.87	TS8	-484.90
TS9	-849.63	TS10	-355.24
TS11	-611.28	TS12	-1996.33
TS13	-1793.94	H_2O	1606.80



R TS1 P1 TS2

P2 TS3 TS4 IM1

TS5 TS6 P3 TS7

IM2 TS8 IM3 TS9

IM4 TS10 P4 IM5

TS12 IM6 TS11 TS13

P5 H_2O

Figure S1. Optimized geometries of species.

Specific pathways resolutions of cellulose hydrolysis

In pathway 1, R→TS1→P1, the decomposition of D-glucopyranose started with the opening of pyran ring, and C(1)-O(7) bond broke, while C(5)-O(7) bond formed a double bond, and fructose obtained. TS1 connected with reactant and product. The energy barrier of pathway 1 was 249.23 KJ/mol.

In pathway 2, R→TS2→P2→TS3→P1, after opening the pyran ring of D-glucopyranose, C(1)-O(7) bond broke. Then, hydroxyl on C(5) transferred into aldehyde group, and glucose formed, in which the hydroxyl on C(2) was oxidized, and the aldehyde group on C(1) was reduced. Finally, fructose generated by the transition state TS3. The energy barrier of pathway 2 was 140.80 KJ/mol.

In pathway 3, R→TS2→P2→TS4→IM1→TS5→P1. Firstly, glucose formed through the transition state TS2. Then, the hydrogen on C(1) was enolized and transferred to the carbonyl group, and the single bond between C(1) and C(2) became double bond. Thereafter, enol form IM1 producted, in which C(2) hydroxyl was oxidized, forming fructose by transition state TS6. The energy barrier of pathway 3 was 286.62 KJ/mol.

In pathway 4, R→TS2→P2→TS4→IM1→TS6→P3. The pathway of forming IM1 was the same as pathway 3. Then, the hydrogen atom on the hydroxyl of C(1) returned to the staggered position on C(2), forming mannose. The energy barrier of pathway 4 was 286.62 KJ/mol.

Pathway 5 was based on pathway 2, and fructose further converted. The carbonyl on C(5) reacted with C(2) hydroxyl, forming furan fructose (IM2). The hydrogen atom on C(1) of IM2 was dehydrated with the hydroxyl on C(2), and a double bond was formed, generating enol form IM3 by transition state TS8. Thereafter, the enol hydrogen on IM3 reacted with hydroxyl on C(3), and transition state TS9 obtained. TS9 removed a molecule of water, forming IM4 contained double bond between C(2) and C(3), which further removed a molecule of water, and 5-HMF obtained. The reaction energy barrier of pathway 5 was 221.54 KJ/mol.

In pathway 6, after the generation of glucose, [2,4] retro-aldol reaction of glucose occurred, and C(2)-C(3) bond broke, forming erthyrose (IM5) and glycolaldehyde (IM6). Erthyrose further conducted [2,2] retro-aldol reaction, and C(4)-C(5) bond broke, formimg glycolaldehyde, which was oxidized into GlycA through the transition state TS13. The energy barrier of pathway 6 was 341.43 KJ/mol.