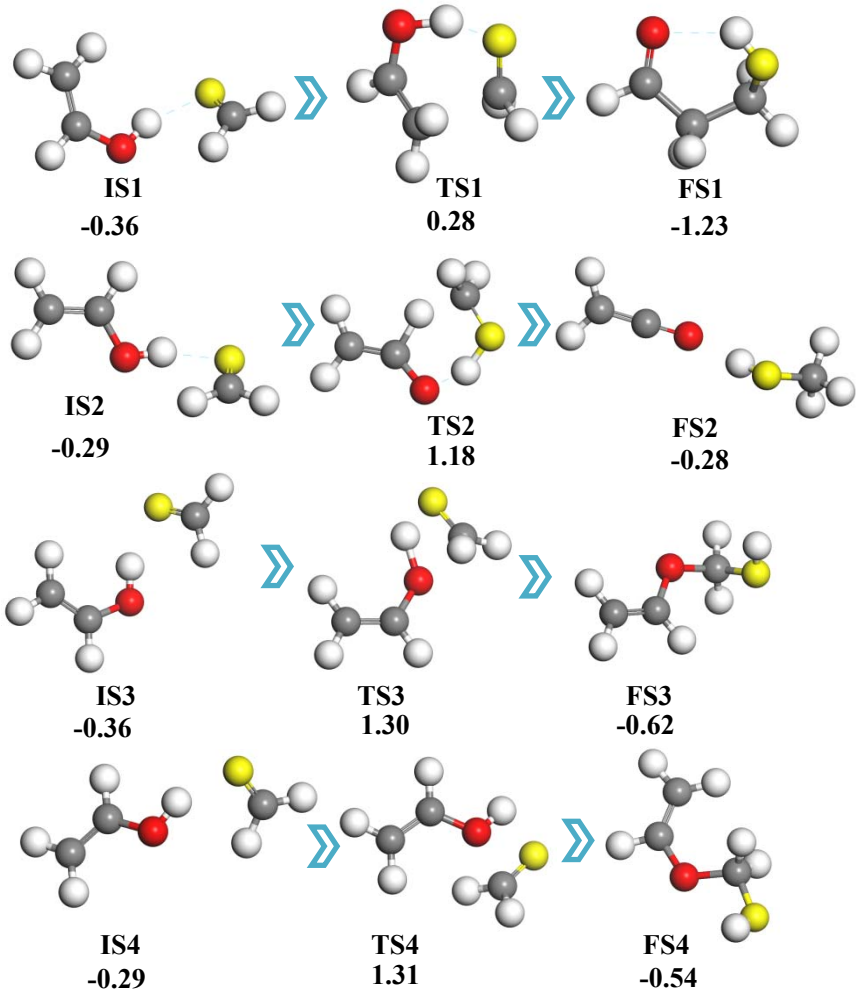
Supplementary information

Reaction Sampling and Reactivity Prediction Using Stochastic Surface Walking Method

Xiao-Jie Zhang, Zhi-Pan Liu*

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Key Laboratory of Computational Physical Science (Ministry of Education), Fudan University, Shanghai 200433, China

Vinyl alcohol and formaldehyde recombination



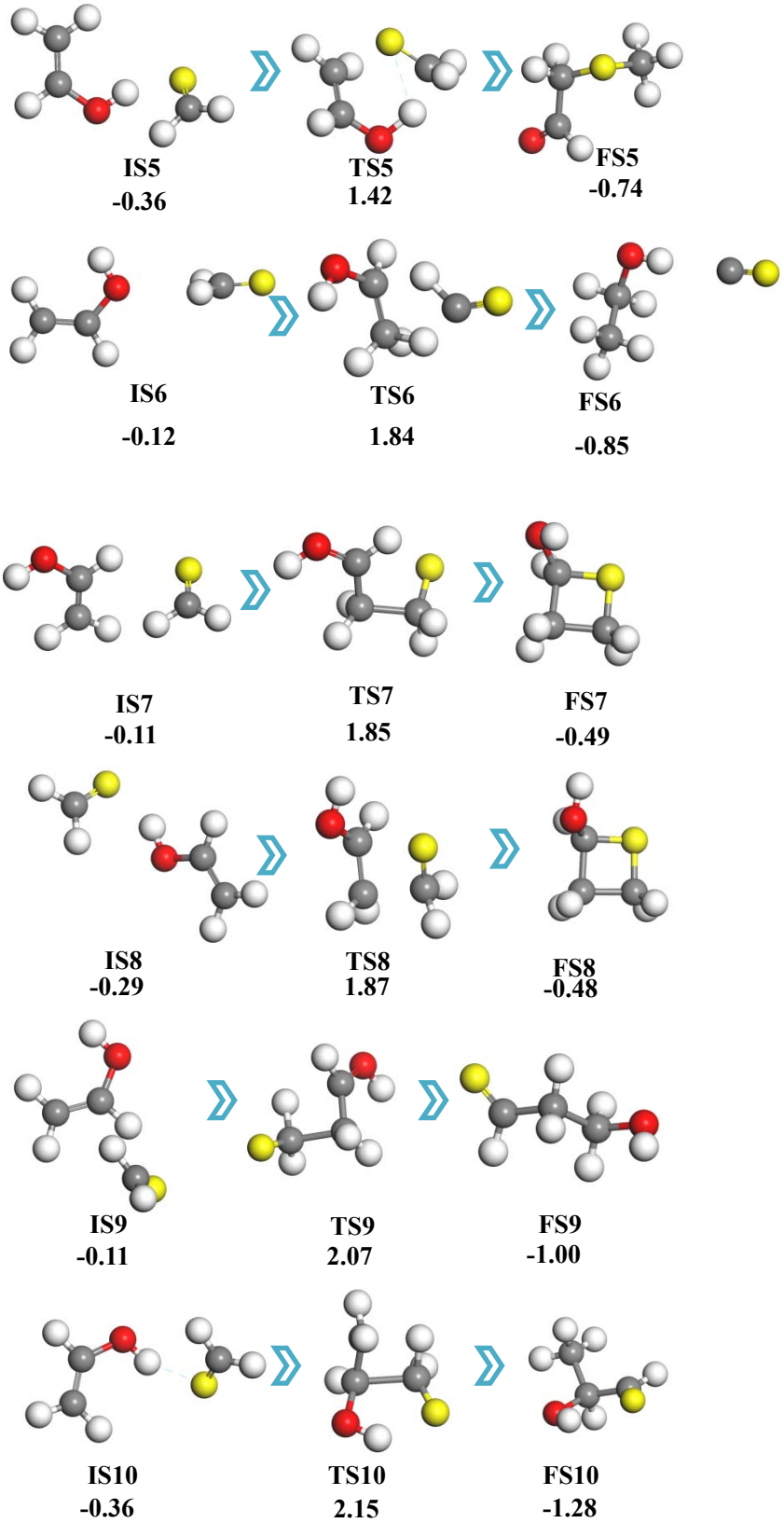


Figure S1 Reaction snapshots (IS, TS and FS) and energetics (in eV) for the ten low energy pathways in vinyl alcohol and formaldehyde recombination

Epoxypropane hydrolysis

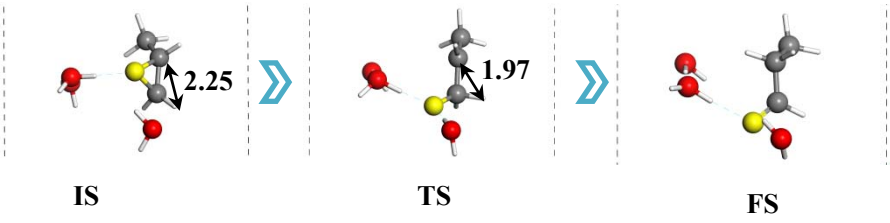


Figure S2 Reaction snapshots for the Epo-P2 pathway obtained from SSW-RS. Key distances (in Å) are labeled.

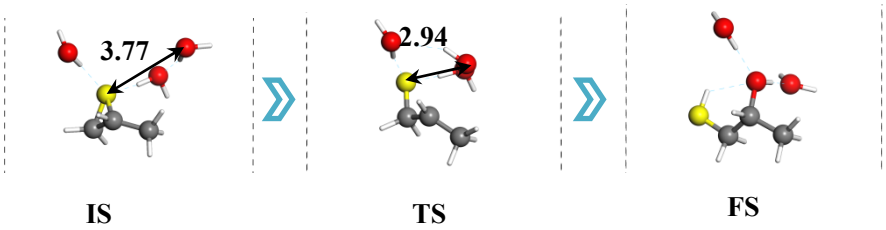


Figure S3 Reaction snapshots for the Epo-P3 pathway obtained from SSW-RS. Key distances (in Å) are labeled.

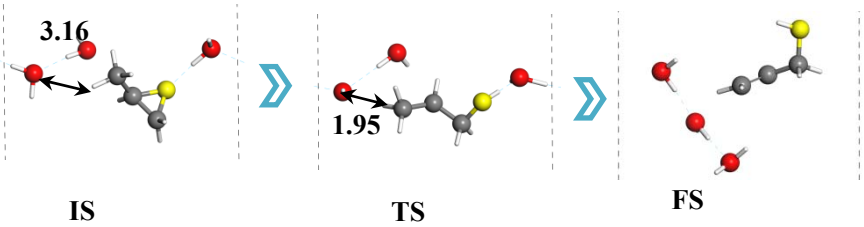


Figure S4 Reaction snapshots for the Epo-P4 pathway obtained from SSW-RS. Key distances (in Å) are labeled.

β-D-glucopyranose decomposition

For the β-D-glucopyranose system, we have obtained 354 minima of β-D-glucopyranose with different conformations, together with 156 pathways from 8 parallel running SSW-RS trajectories. Below we show the energy distribution of these conformation isomers calculated using PBE functional and NAO basis (SIESTA), which expands more than 1 eV starting from the GM. We also show the typical structural conformations in Figure S5, featuring with different H-bonding network. We can see that above 0.3 eV, the energy of the conformation isomers is already rather close, forming continuous-like spectrum. This indicates that SSW-RS is able to sample low energy intermediate structures with various H-bonding network. The conformations reported in Figure 8 (for the reactions) are only those initial states that are related to the low energy pathways.

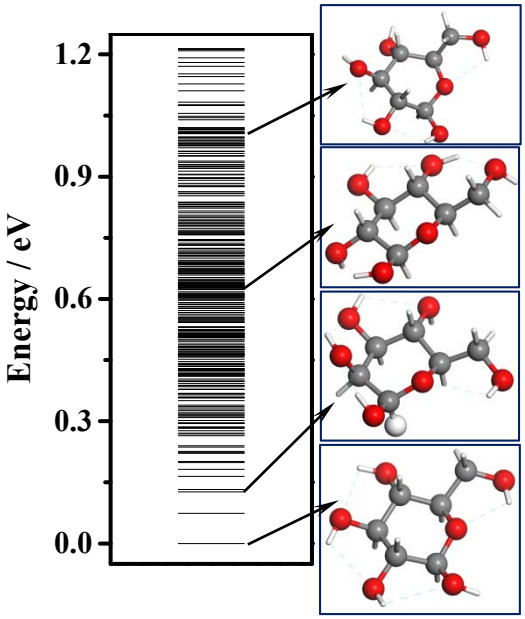


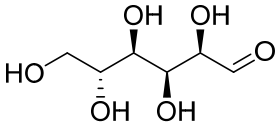
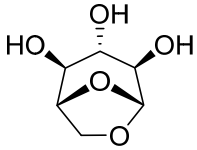
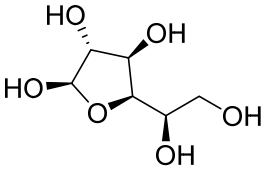
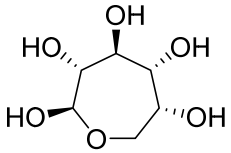
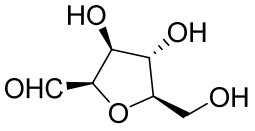
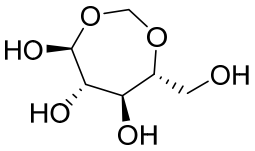
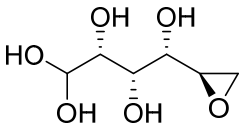
Figure S5 The configuration energy spectrum of β-D-glucopyranose obtained from SSW-RS. Grey: C atom, Red: O atom; White: H atom

Table S1 The SSW-RS results for the β-D-glucopyranose decomposition, including all the 15 possible products identified (the first five products are discussed in the main text, see Table 1).

[#] N_{path} is the number of pathways to produce the target product identified from SSW-RS;

[$] N_{tot} equal to 156, being the total number of pathways obtained from SSW-RS;

[*] N_{SSW} equal to 3376, being the total number of SSW steps.

Product	N_{path}[#]	N_{path}/N_{tot}[$]	N_{path}/N_{SSW}[*]
	16	16%	0.47%
	10	10%	0.30%
	14	14%	0.41%
	11	11%	0.33%
	3	3%	0.09%
	1	1%	0.03%
	1	1%	0.03%

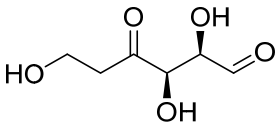
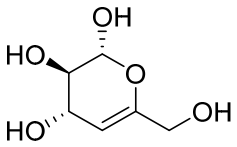
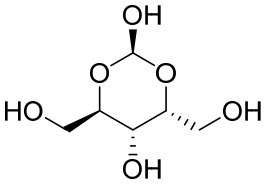
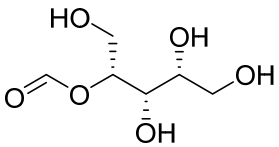
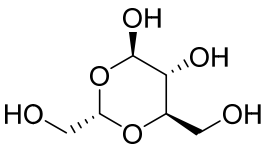
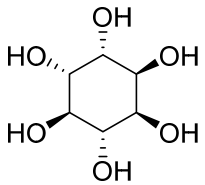
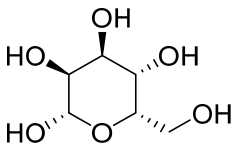
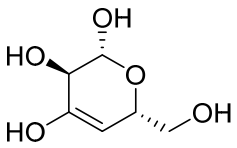
	1	1%	0.03%
	1	1%	0.03%
	1	1%	0.03%
	1	1%	0.03%
	1	1%	0.03%
	3	3%	0.09%
	1	1%	0.03%
	1	1%	0.03%

Table S2 Reaction free energy barrier and free energy obtained by M06-2X/ aug-cc-pvtz method

Pathway	$\Delta_r H^{TS}_{800K}$ /eV	$\Delta_r G^{TS}_{800K}$ /eV	$\Delta_r H^{FS}_{800K}$ /eV	$\Delta_r G^{FS}_{800K}$ /eV
1	1.52	1.82	0.73	0.65
2	2.23	2.26	0.14	0.18
3	2.38	2.61	0.60	0.61
4	2.50	2.56	0.35	0.46
5	3.14	3.06	0.43	-0.03