Supporting Information

A coupled Density Functional Theory-Microkinetic modeling for the hydrodeoxygenation of glycerol to propylene on MoO_3

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Totals: 10 pages, 5 schemes, 1 figure, and 2 tables

Table of contents

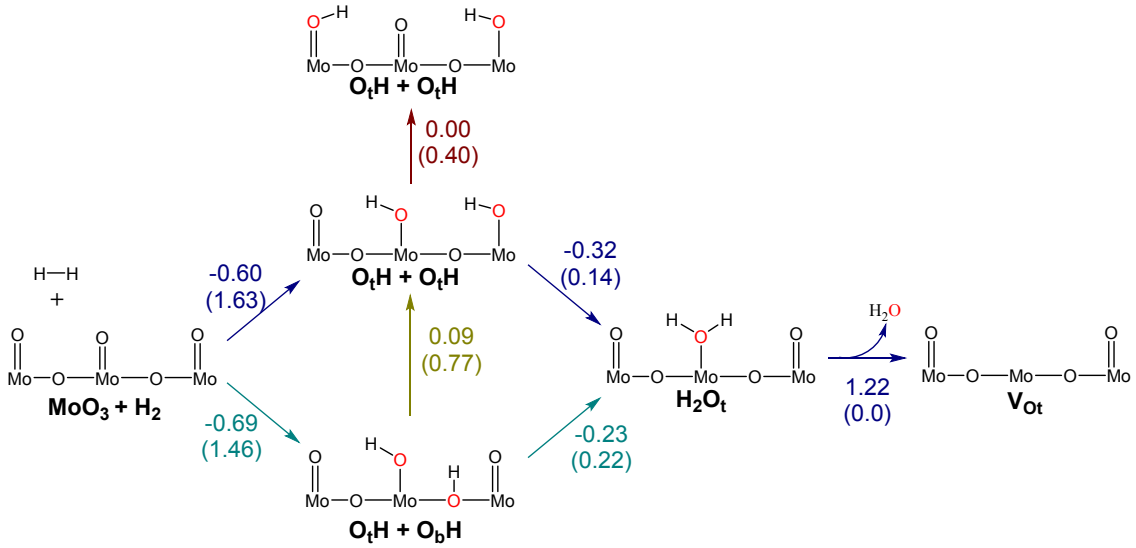
S1. ioChem-BD

All geometries of gas phase, adsorption, and transition states structures have been uploaded in to the ioChem-BD platform. They can be reviewed through the following link: https://iochem-bd.iciq.es/browse/review-collection/100/9609/924ff88c4a4bb24df1dccc53.

Instructions:

1. Copy the link or DOI in your browse.
2. Choose the structure that you want to check and click in its title. The structure will open.
3. You can move the structure with the mouse.
4. To measure bond distances or angles double click on the first atom and single click on the others. The bond distances or angles will be displayed.
5. Click on View data to see all the information of the job. All the input and output data are shown.
6. To obtain atomic coordinates click on Download geometry.
7. The input and output files can be download click on Download box at the left of the screen.

S2. Vacancy formation and hydrogen diffusion



Scheme S1. Scheme for hydrogen adsorption, hydrogen diffusion, and vacancy formation. Reaction energies for each elementary step are shown, ΔE in eV; between brackets are presented the energy barriers, E_a in eV.

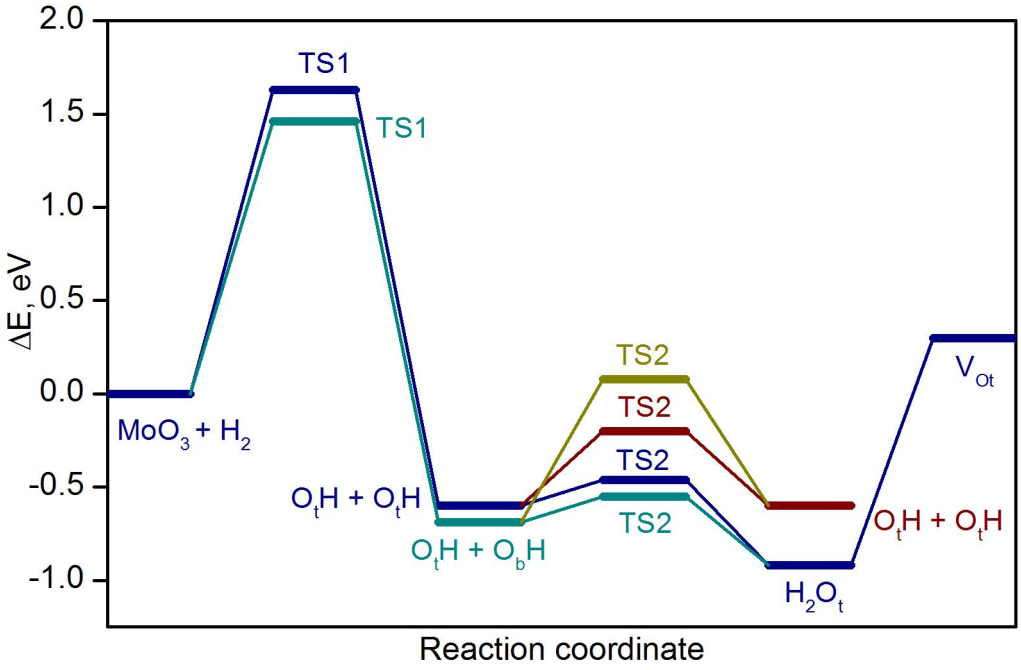


Figure S1. Reaction energy profile for hydrogen adsorption and diffusion and for vacancy formation.

S3. Hydrodeoxygenation (HDO) reaction network

Table S1. Numeric code for reactions in Figure 2 of the main text.

No.	Reaction
1	GlycerolH*(a) + O_t → Glycerol*(a) + O_tH
2	Glycerol*(a) + O_b → 1,2-EnolH(a) + O_bH
3	GlycerolH*(b) + O_t → Glycerol*(b) + O_tH
4	Glycerol*(b) + O_b → 1,3-EnolH(b) + O_bH
5	PGH*(a) + O_t → PG*(a) + O_tH
6	PG*(a) + O_b → Propen-2-olH(a) + O_bH
7	PGH*(b) + O_t → PG*(b) + O_tH
8	PG*(b) + O_b → 1-Propenol(b) + O_bH
9	PGH*(b) + O_t → PG*(b) + O_tH
10	PG*(b) + O_b → 2-PropenolH(b) + O_bH + O_t
11	HPH*(b) + O_t → HP*(b) + O_tH
12	HP*(b) + O_b → Acrolein(a) + O_bH
13	1,3-Propanediol* + O_tH → 1,3-PropanediolH* + O_t
14	1,3-Propanediol* + O_b → 2-PropenolH(a) + O_bH
15	2-PropanolH* + O_t → 2-Propanol* + O_tH
16	2-Propanol* + O_b → Propylene + O_bH
17	1-PropanolH* + O_t → 1-Propanol* + O_tH
18	1-Propanol* + O_b → Propylene + O_bH
19	1,2-EnolH * + O_t → 1,2-Enol* + O_tH
20	1,2 -Enol* + O_tH → Acetol* + O_t
21	1,3-EnolH * + O_t → 1,3-Enol* + O_tH
22	1,3-Enol* + O_tH → HPH*(a) + O_t
23	Propen-2-olH * + O_t → Propen-2-ol* + O_tH
24	Propen-2-ol * + O_tH → Propanone* + O_t
25	1-PropenolH * + O_t → 1-Propenol* + O_tH
26	1-Propenol * + O_tH → Propanal* + O_t
27	Acetol* + O_tH → PG* + O_t
28	PG* + O_tH → PGH*(b) + O_t
29	HPH*(a) + O_tH → 1,3-Propanediol* + O_t
30	1,3-Propanediol* + O_tH → 1,3-PropanediolH*+ O_t
31	Acrolein* + O_tH → 2-Propenol* + O_t
32	2-Propenol* + O_tH → 2-PropenolH* + O_t
33	Acrolein* + O_tH → 1-Propenol* + O_t
34	1-Propenol * + O_tH → 1-PropenolH* + O_t
35	Propanone* + O_tH → 2-Propanol* + O_t

36	2-Propanol * + O_tH → 2-PropanolH* + O_t
37	Propanal* + O_tH → 1-Propanol* + O_t
38	1-Propanol * + O_tH → 1-PropanolH* + O_t
39	2-PropenolH* + O_t → 2-Propenol* + O_tH
40	2-Propenol* + O_t → Propylene + O_tH

Table S2. Reaction energies, ΔE; direct energy barriers, $E_{a,d}$; and reverse energy barriers, $E_{a,r}$, in eV, for all the elementary steps of the reaction network. Energies corrected by ZPVE. The imaginary frequency for all the transition states, ν_i, is in cm^{-1}.

Reaction list	ΔE	$E_{a,d}$	$E_{a,r}$	ν_i
Glycerol →1,2-Enol				
GlycerolH(g) + * → GlycerolH*(a)	-1.72			
GlycerolH*(a) + O_t → Glycerol*(a) + O_tH	0.51	0.72	0.21	861
Glycerol*(a) + O_b → 1,2-EnolH(a) + O_bH	-0.08	1.13	1.21	926
1,2-EnolH(a) → 1,2-EnolH(g) + O_t	0.60			
Glycerol → 1,3-Enol				
GlycerolH(g) + * → GlycerolH*(b)	-1.92			
GlycerolH*(b) + O_t → Glycerol*(b) + O_tH	0.45	0.80	0.35	964
Glycerol*(b) + O_b → 1,3-EnolH(b) + O_bH	0.15	1.29	1.14	926
1,3-EnoHl(b) → 1,3-EnolH(g) + O_t	0.65			
1,2-Enol → Acetol				
1,2-EnolH(g) + * → 1,2-EnolH*	-1.59			
1,2-EnolH * + O_t → 1,2-Enol* + O_tH	0.30	0.68	0.37	434
1,2 -Enol* + O_tH → Acetol* + O_t	-1.03	0.09	1.12	931
Acetol* → Acetol(g) + *	1.67			
1,3-Enol → Hydroxypropanal				
1,3-EnolH(g) + * → 1,3-EnolH*	-1.20			
1,3-EnolH * + O_t → 1,3-Enol* + O_tH	0.17	0.38	0.21	655
1,3-Enol* + O_tH → HPH*(a) + O_t	-0.86	-0.04	0.82	808
HPH*(a) → HPH(g) + *	1.69			
Acetol → Propylene Glycol				
Acetol(g) + * → Acetol*	-1.83			
Acetol* + O_tH → PG* + O_t	0.20	1.43	1.23	1322
PG* + O_tH → PGH*(b) + O_t	-0.46	0.25	0.71	783
PGH*(b) → PGH(g) + *	1.85			
Hydroxypropanal → 1,3-Propanediol				
HPH(g) + * → HPH*(a)	-2.16			
HPH*(a) + O_tH → 1,3-Propanediol* + O_t	0.22	1.45	1.22	1390
1,3-Propanediol* + O_tH → 1,3-PropanediolH* + O_t	-0.29	0.22	0.51	834
1,3-PropanediolH* → 1,3-PropanediolH(g) + *	1.59			
Hydroxypropanal → Acrolein				
HPH(g) + * → HPH*(b)	-1.55			

HPH*(b) + O_t → HP*(b) + O_tH	0.18	0.50	0.32	754
HP*(b) + O_b → Acrolein(a) + O_bH	0.23	1.42	1.19	1069
Acrolein*(a) → Acrolein(g) + O_t	0.52			
Propylene Glycol → Propen-2-ol				
PGH(g) + * → PGH*(a)	-1.51			
PGH*(a) + O_t → PG*(a) + O_tH	0.26	0.44	0.19	557
PG*(a) + O_b → Propen-2-olH(a) + O_bH	0.06	1.05	0.99	1174
Propen-2-olH(a) → Propen-2-olH(g) + O_t	0.42			
Propylene Glycol → 1-Propenol				
PGH(g) + * → PGH*(b)	-1.83			
PGH*(b) + O_t → PG*(b) + O_tH	0.46	0.67	0.22	941
PG*(b) + O_b → 1-Propenol(b) + O_bH	0.24	1.34	1.09	643
1-Propenol(b) → 1-PropenolH(g) + O_t	0.49			
Propylene Glycol → 2-Propenol				
PGH(g) + * → PGH*(b)	-1.83			
PGH*(b) + O_t → PG*(b) + O_tH	0.45	0.67	0.22	941
PG*(b) + O_b → 2-PropenolH(b) + O_bH + O_t	0.45	1.47	1.03	643
2-PropenolH(b) → 2-PropenolH(g)	0.66			
1,3-Propanediol → 2-Propenol				
1,3-PropanediolH(g) + * → 1,3-PropanediolH*	-1.62			
1,3-PropanediolH* + O_t → 1,3-Propanediol*+ O_tH	0.34	0.65	0.31	876
1,3-Propanediol* + O_b → 2-PropenolH(a) + O_bH	0.32	1.59	1.27	1055
2-PropenolH(a) → 2-PropenolH(g) + O_t	0.66			
Acrolein → 2-Propenol				
Acrolein(g) + * → Acrolein*	-1.90			
Acrolein* + O_tH → 2-Propenol* + O_t	0.33	1.09	0.76	949
2-Propenol* + O_tH → 2-PropenolH* + O_t	-0.20	0.25	0.46	693
2-PropenolH* → 2-PropenolH(g) + *	1.40			
Acrolein → 1-Propenol				
Acrolein(g) + * → Acrolein*	-1.90			
Acrolein* + O_tH → 1-Propenol* + O_t	-0.11	1.18	1.29	1096
1-Propenol * + O_tH → 1-PropenolH* + O_t	-0.12	0.26	0.38	615
1-PropenolH* → 1-PropenolH(g) + *	1.41			
Propen-2-ol → Propanone				
Propen-2-olH(g) + * → Propen-2-olH*	-1.37			
Propen-2-olH * + O_t → Propen-2-ol* + O_tH	0.04	0.42	0.38	863
Propen-2-ol * + O_tH → Propanone* + O_t	-0.95	0.54	1.49	864
Propanone* → Propanone(g) + *	1.73			
1-Propenol → Propanal				
1-PropenolH(g) + * → 1-PropenolH*	-1.41			
1-PropenolH * + O_t → 1-Propenol* + O_tH	0.12	0.38	0.26	615
1-Propenol * + O_tH → Propanal* + O_t	-0.68	0.01	0.68	926
Propanal* → Propanal (g) + *	1.61			
Propanone → 2-Propanol				
Propanone(g) + * → Propanone*	-2.02			
Propanone* + O_tH → 2-Propanol* + O_t	0.37	1.44	1.07	1227

2-Propanol * + O_tH → 2-PropanolH* + O_t	-0.34	0.40	0.74	1050
2-PropanolH* → 2-PropanolH(g) + *	1.74			
Propanal → 1-Propanol				
Propanal(g) + * → Propanal*	-1.85			
Propanal* + O_tH → 1-Propanol* + O_t	0.19	1.48	1.29	
1-Propanol * + O_tH → 1-PropanolH* + O_t	-0.26	0.20	0.46	751
1-PropanolH* → 1-PropanolH(g) + *	1.52			
2-Propanol → Propylene				
2-PropanolH(g) + * → 2-PropanolH*	-1.75			
2-PropanolH* + O_t → 2-Propanol* + O_tH	0.35	0.74	0.39	557
2-Propanol* + O_b → Propylene + O_bH	0.74	1.51	0.77	742
Propylene → Propylene(g) + O_t	0.23			
1-Propanol → Propylene				
1-PropanolH(g) + * → 1-PropanolH*	-1.51			
1-PropanolH* + O_t → 1-Propanol* + O_tH	0.25	0.44	0.19	816
1-Propanol* + O_b → Propylene + O_bH	0.42	1.25	0.82	945
Propylene → Propylene(g) + O_t	0.23			
2-Propenol → Propylene				
2-PropenolH(g) + * → 2-PropenolH*	-1.41			
2-PropenolH* + O_t → 2-Propenol* + O_tH	0.22	0.45	0.22	671
2-Propenol* + O_t → Propylene + O_tH	-0.14	1.03	1.17	1565
Propylene → Propylene(g) + O_t	0.05			
H_2O formation				
$H_2(g) + 2O_t \rightarrow 2O_tH$	-0.86	1.63	2.49	
$H_2(g) + O_t + O_b \rightarrow O_tH + O_bH$	-0.96	1.46	2.42	
$O_bH + O_t \rightarrow O_b + O_tH$	0.09	0.77	0.68	1148
$2O_tH \rightarrow H_2O_t + O_t$	-0.32	0.14	0.46	647
$H_2O_t \rightarrow H_2O(g) + *$	1.22			

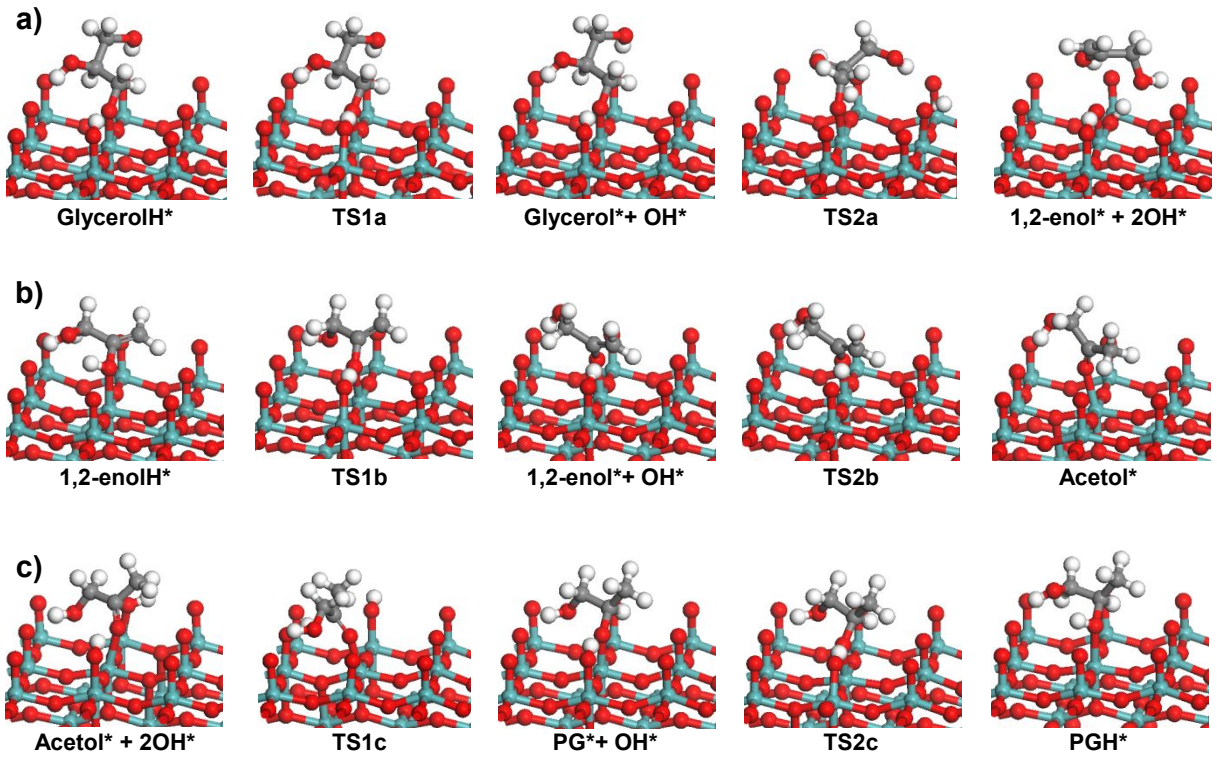
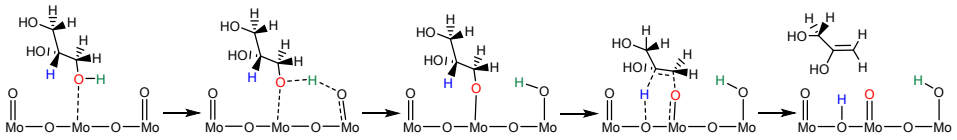
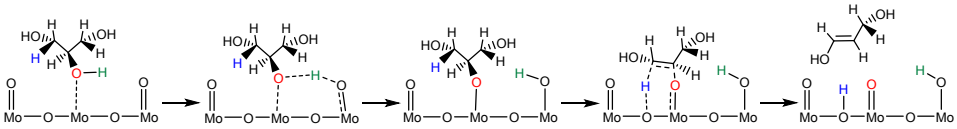


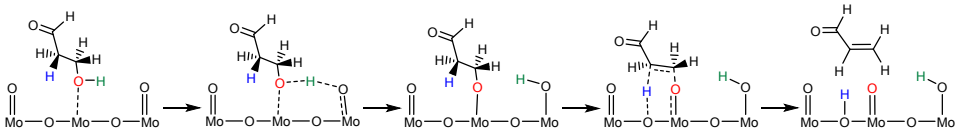
Figure S2. Optimized structures of intermediated and transition states, TS, of a) Glycerol dehydration to 1,2-enol, b) keto-enol equilibrium between 12-enol and acetol, and c) Acetol hydrogenation to propylene glycol, PG.



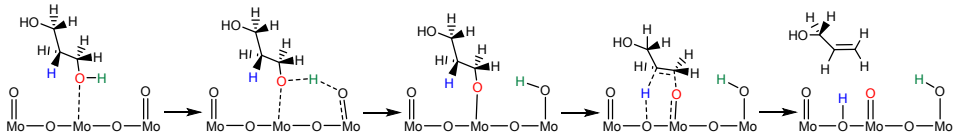
Glycerol → 1,3-enol



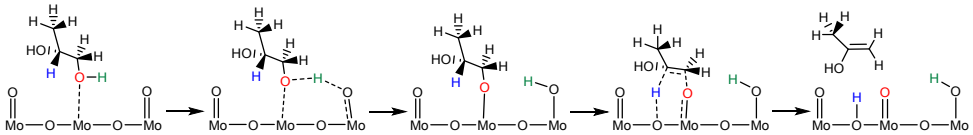
HP → Acrolein



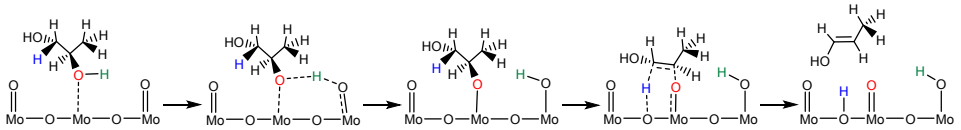
1,3-propanediol → 2-propenol



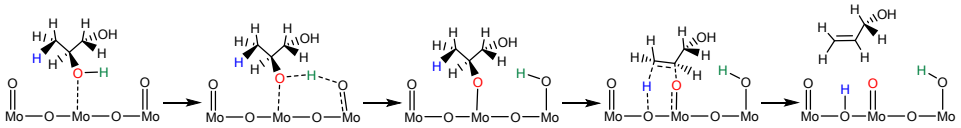
PG → Propen-2-ol



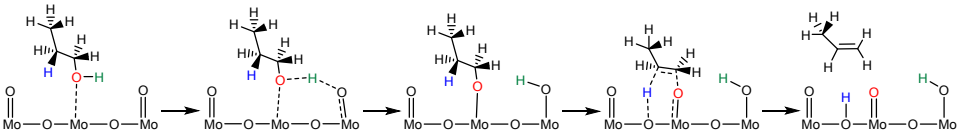
PG → 1-propenol



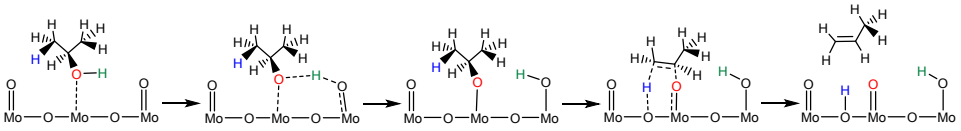
PG → 2-propenol



1-propanol → Propylene

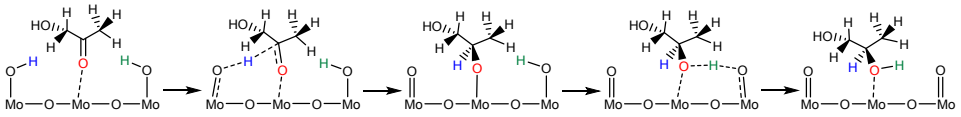


2-propanol → Propylene

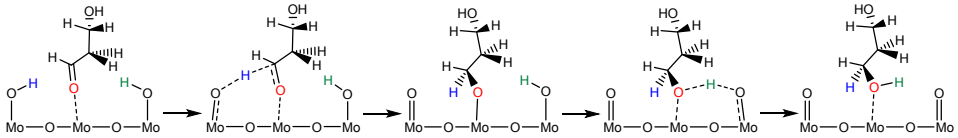


Scheme S2. Reaction mechanism of the dehydration steps in the HDO reaction network.

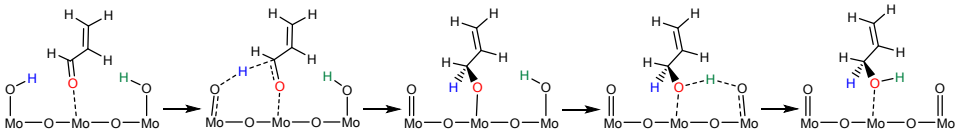
Glycerol → 1,2-enol



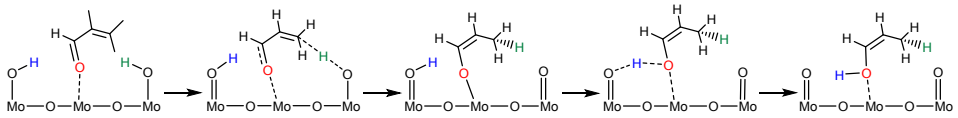
HP → 1,3-propanediol



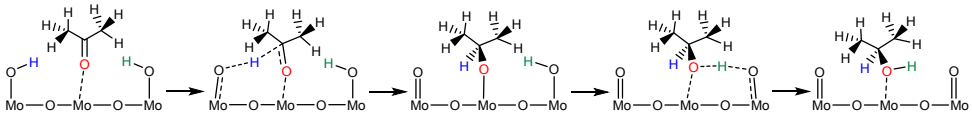
Acrolein → 2-propenol



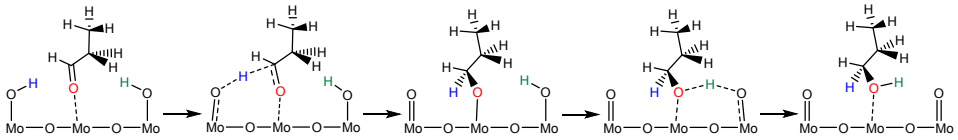
Acrolein → 1-propenol



Propanone → 2-propanol

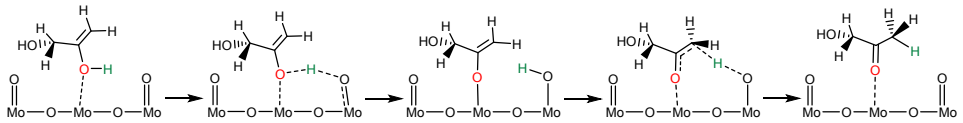


Propanal → 1-propanol

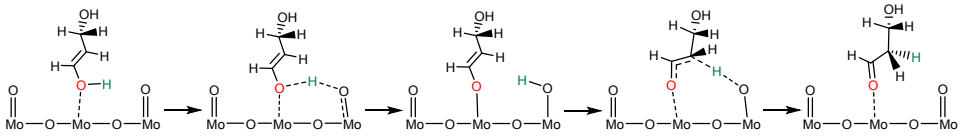


Scheme S3. Reaction mechanism of the hydrogenation steps in the HDO reaction network.

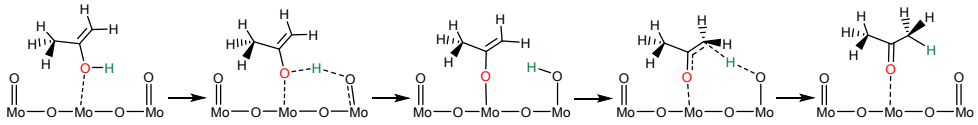
Acetol → PG



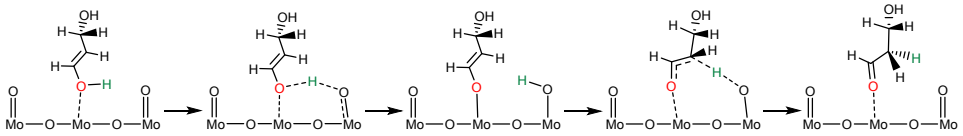
1,3-enol → HP



Propen-2-ol → Propanone

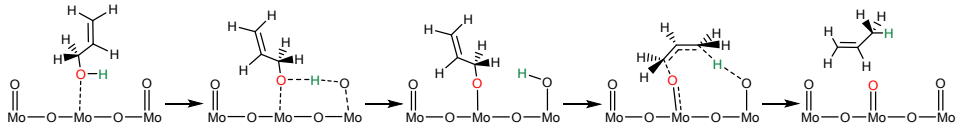


1-propenol → Propanal



Scheme S4. Reaction mechanism of the keto-enol equilibria steps in the HDO reaction network.

1,2-enol → Acetol



Scheme S5. Reaction mechanism of the 2-propenol conversion to propylene in the HDO reaction network.