

Supporting Information

Reaction kinetics of hydrogen addition reactions to methyl butenoate

Yage Gao,^{ab} Xiaoyu Li,^{ab} and Xiaoqing You*^{ab}

^a Center for Combustion Energy, Tsinghua University, Beijing 100084, China

^b Key Laboratory for Thermal Science and Power Engineering of the Ministry of
Education, Tsinghua University, Beijing 100084, China

Corresponding Author:

Xiaoqing You

Center for Combustion Energy

Tsinghua University, Beijing 100084, China

Phone: +86-10-62771854

E-mail: xiaoqing.you@tsinghua.edu.cn

Table S1 The barrier heights (the zero point energy included, ΔE_f : forward barrier height, ΔE_r : backward barrier height) and enthalpies of reaction at 0 K (ΔH_r) of hydrogen addition reactions computed by various quantum chemical methods. Single point calculations were carried out based on the lowest-energy-structures optimized at the M08-HX/MG3S level of theory, and zero point energies (ZPEs) were calculated using scaled harmonic frequencies with a scale factor of 0.973.^a (in kcal/mol)

a) Methyl 3-butenolate

	R _{1,1}			R _{2,1}			R _{3,1}			R _{4,1}			MUD ^b
	ΔH_r	ΔE_f	ΔE_r	ΔH_r	ΔE_f	ΔE_r	ΔH_r	ΔE_f	ΔE_r	ΔH_r	ΔE_f	ΔE_r	
CCSD(T)-F12a/jun-cc-pVTZ	-6.7	13.8	20.5	0.7	11.1	10.4	-33.5	4.0	37.5	-36.1	2.5	38.6	
M06-2x/ma-TZVP	-0.6	-0.6	0.1	-0.7	-0.4	0.3	0.0	1.0	1.0	-0.4	0.9	1.3	0.6
MN15/ma-TZVP	-1.3	-1.7	-0.4	-0.6	-0.6	0.0	0.2	0.7	0.5	-0.6	0.5	1.1	0.7
MN12-L/MG3S	-0.2	-1.1	-0.9	-0.9	-0.7	0.2	0.6	0.9	0.3	-1.1	0.4	1.4	0.7
MN15/MG3S	-1.6	-1.4	0.3	-0.6	-0.8	-0.2	0.2	0.8	0.6	-0.6	0.5	1.1	0.7
MN12-SX/ma-TZVP	-0.8	-0.7	0.1	-2.0	-1.5	0.5	0.1	-0.1	-0.2	-1.4	-0.6	0.8	0.7
M08-HX/ma-TZVP	-0.8	-0.6	0.2	-0.3	-0.8	-0.4	-0.8	0.7	1.5	-1.2	0.5	1.7	0.8
M06-2X/MG3S	-1.1	-0.2	0.9	-1.1	-0.6	0.5	-0.2	1.0	1.3	-0.7	1.0	1.6	0.8
MN12-SX/MG3S	-1.5	-0.6	0.9	-1.9	-1.9	0.0	-0.3	-0.4	-0.1	-1.5	-0.8	0.7	0.9
MN12-L/ma-TZVP	0.3	-1.3	-1.7	-1.0	-0.4	0.6	0.8	1.1	0.4	-1.1	0.5	1.6	0.9
M08-SO/ma-TZVP	-0.1	-0.1	0.1	-0.9	-0.8	0.2	-1.4	0.7	2.1	-2.2	0.4	2.7	1.0
SOGGA11-X/MG3S	0.7	0.4	-0.2	-2.4	0.4	2.9	-0.5	0.5	1.0	-1.5	-0.1	1.4	1.0
M11/ma-TZVP	-1.7	-1.3	0.4	0.8	-0.9	-1.6	-0.8	0.0	0.9	-2.0	-0.2	1.7	1.0
M08-HX/MG3S	-1.5	-0.5	1.1	-0.8	-1.1	-0.3	-1.2	0.6	1.8	-1.6	0.4	2.0	1.1
M08-SO/MG3S	-1.0	-0.2	0.8	-1.1	-1.0	0.1	-1.5	0.6	2.1	-2.3	0.4	2.6	1.1
SOGGA11-X/ma-TZVP	1.6	0.5	-1.1	-2.3	0.7	3.0	-0.4	0.6	1.0	-1.5	0.0	1.4	1.2
M11/MG3S	-2.8	-1.4	1.4	0.0	-1.0	-1.0	-1.4	0.0	1.4	-2.4	-0.2	2.1	1.3
PWB6K/ma-TZVP	-0.2	0.4	0.6	-2.7	0.6	3.3	-1.1	0.5	1.7	-2.1	0.0	2.1	1.3
MN15-L/MG3S	2.6	0.0	-2.5	1.3	-0.9	-2.3	-0.7	0.9	1.5	-1.4	0.5	1.9	1.4
M06/MG3S	1.4	0.8	-0.6	0.8	1.0	0.2	-1.7	0.9	2.5	-3.0	0.7	3.7	1.4
PWB6K/MG3S	-0.7	0.5	1.3	-2.8	0.5	3.3	-1.3	0.6	1.8	-2.2	0.1	2.3	1.5
MN15-L/ma-TZVP	3.1	-0.5	-3.6	1.2	-0.7	-1.8	-0.6	0.9	1.5	-1.4	0.5	1.9	1.5
M05-2X/ma-TZVP	-0.8	1.1	1.9	-1.5	1.2	2.7	-0.4	1.8	2.2	-0.7	1.7	2.4	1.5
M11-L/ma-TZVP	0.3	-2.8	-3.1	0.5	0.2	-0.3	-0.1	1.9	2.0	-2.5	1.3	3.8	1.6
ω B97XD/ma-TZVP	0.2	0.5	0.3	-1.5	1.0	2.5	-1.6	1.4	3.0	-2.5	0.9	3.4	1.6
M11-L/MG3S	-0.7	-2.9	-2.3	0.3	-0.2	-0.4	-0.8	1.6	2.4	-3.2	1.0	4.2	1.7
M06/ma-TZVP	2.4	0.8	-1.5	0.7	1.3	0.6	-1.5	1.1	2.5	-3.1	0.8	3.9	1.7
ω B97XD/MG3S	-0.4	0.6	1.0	-1.6	0.9	2.5	-1.8	1.4	3.2	-2.6	1.0	3.6	1.7
B3LYP/MG3S	-1.0	-4.5	-3.5	-2.7	-2.0	0.8	-0.8	-1.6	-0.8	-2.0	-2.2	-0.2	1.8
B3LYP/ma-TZVP	-0.5	-4.6	-4.2	-2.6	-1.9	0.8	-0.7	-1.7	-1.0	-1.9	-2.3	-0.4	1.9
M05-2X/MG3S	-1.4	1.6	3.0	-2.0	1.0	3.0	-0.7	2.0	2.6	-0.9	1.9	2.8	1.9
ω B97X/ma-TZVP	0.6	2.6	1.9	-1.6	2.4	4.0	-2.0	2.6	4.6	-3.0	2.1	5.1	2.7
ω B97X/MG3S	-0.1	2.7	2.8	-1.7	2.3	4.0	-2.2	2.6	4.8	-3.1	2.2	5.3	2.8
ω B97/ma-TZVP	1.2	4.2	3.1	-1.5	3.7	5.1	-2.7	3.6	6.3	-3.5	3.1	6.7	3.7
ω B97/MG3S	0.4	4.3	3.9	-1.6	3.4	5.1	-2.9	3.6	6.4	-3.6	3.1	6.8	3.7

b) Methyl 2-butenate

	R _{5,1}			R _{6,1}			R _{7,1}			R _{8,1}			MUD ^b	MMUD ^c
	ΔH_r	ΔE_f	ΔE_r	ΔH_r	ΔE_f	ΔE_r	ΔH_r	ΔE_f	ΔE_r	ΔH_r	ΔE_f	ΔE_r		
CCSD(T)-F12a/jun-cc-pVTZ	-17.6	12.0	29.6	4.3	12.4	8.1	-33.5	3.6	37.1	-37.7	3.2	40.9		
M06-2X/ma-TZVP	-1.6	-0.8	0.8	-0.9	-0.4	0.4	-0.3	0.4	0.7	-0.4	0.6	1.0	0.7	0.7
SOGGA11-X/ma-TZVP	0.0	0.2	0.2	-1.6	0.3	1.9	-0.4	1.0	1.4	-0.4	0.8	1.2	0.8	1.0
MN15/ma-TZVP	-3.4	-1.7	1.6	-0.7	-0.7	0.0	0.0	0.4	0.4	-0.3	0.3	0.5	0.8	0.8
MN15-L/MG3S	0.4	-0.6	-1.1	1.8	-1.0	-2.8	0.3	0.3	0.1	-0.8	0.1	1.0	0.9	1.1
M08-HX/ma-TZVP	-2.2	-0.7	1.5	-0.6	-0.9	-0.4	-0.9	0.3	1.2	-0.5	0.4	0.9	0.9	0.8
SOGGA11-X/MG3S	-0.8	0.2	1.0	-1.8	0.0	1.8	-0.5	0.8	1.3	-0.5	0.6	1.1	0.9	0.9
MN12-L/ma-TZVP	-3.1	-2.0	1.2	-0.4	-0.7	-0.3	1.2	1.0	-0.3	0.6	0.6	0.0	0.9	0.9
MN15/MG3S	-3.9	-1.5	2.4	-0.7	-0.9	-0.3	0.1	0.4	0.3	-0.3	0.3	0.6	1.0	0.8
MN15-L/ma-TZVP	0.9	-1.1	-2.0	1.6	-0.8	-2.4	0.3	0.4	0.1	-0.7	0.3	1.0	1.0	1.2
M06-2X/MG3S	-2.3	-0.5	1.8	-1.3	-0.6	0.7	-0.5	0.5	0.9	-0.7	0.6	1.3	1.0	0.9
MN12-L/MG3S	-3.4	-1.8	1.6	-0.3	-1.0	-0.7	1.1	0.6	-0.5	0.4	0.2	-0.2	1.0	0.9
MN12-SX/ma-TZVP	-3.4	-1.4	2.0	-1.7	-1.5	0.2	-0.2	-0.4	-0.2	-0.2	-0.8	-0.6	1.0	0.9
M08-HX/MG3S	-2.9	-0.7	2.3	-1.0	-1.2	-0.2	-1.2	0.1	1.3	-0.9	0.2	1.1	1.1	1.1
M08-SO/ma-TZVP	-1.8	-0.3	1.6	-1.0	-0.9	0.1	-2.0	0.3	2.3	-1.9	0.1	2.1	1.2	1.1
MN12-SX/MG3S	-3.9	-1.3	2.6	-1.6	-1.9	-0.4	-0.5	-0.7	-0.3	-0.4	-1.2	-0.7	1.3	1.1
M08-SO/MG3S	-2.7	-0.4	2.3	-1.0	-1.1	-0.1	-2.0	0.2	2.2	-2.1	0.0	2.1	1.3	1.2
M06/ma-TZVP	-1.0	0.5	1.5	1.1	0.7	-0.5	-1.8	1.1	2.9	-1.5	1.2	2.6	1.4	1.5
M11/ma-TZVP	-3.4	-1.3	2.1	0.6	-1.1	-1.7	-1.8	-0.6	1.2	-1.4	-0.1	1.2	1.4	1.2
M11-L/ma-TZVP	-2.0	-2.8	-0.8	1.1	-0.6	-1.7	-0.8	1.6	2.4	0.1	1.8	1.6	1.4	1.5
M06/MG3S	-1.7	0.5	2.2	1.4	0.3	-1.0	-1.8	0.9	2.7	-1.6	0.9	2.5	1.4	1.4
PWB6K/ma-TZVP	-2.2	0.2	2.4	-2.5	0.4	2.8	-1.3	0.5	1.8	-1.1	0.5	1.6	1.5	1.4
B3LYP/MG3S	-2.0	-4.4	-2.4	-1.9	-2.7	-0.9	-0.7	-1.0	-0.3	-0.9	-1.2	-0.4	1.6	1.7
M11-L/MG3S	-2.7	-3.0	-0.3	0.9	-1.0	-1.9	-1.5	1.1	2.7	-0.6	1.4	2.0	1.6	1.6
B3LYP/ma-TZVP	-1.4	-4.5	-3.1	-1.7	-2.6	-0.9	-0.7	-1.1	-0.5	-0.8	-1.3	-0.5	1.6	1.7
PWB6K/MG3S	-2.8	0.3	3.0	-2.6	0.2	2.8	-1.4	0.5	1.9	-1.3	0.5	1.8	1.6	1.5
M11/MG3S	-4.5	-1.5	3.0	-0.3	-1.3	-1.0	-2.2	-0.7	1.5	-1.9	-0.2	1.6	1.6	1.5
ωB97XD/ma-TZVP	-1.7	0.5	2.2	-1.2	0.5	1.7	-2.0	1.5	3.5	-2.1	1.6	3.6	1.8	1.7
M05-2X/ma-TZVP	-2.5	1.2	3.7	-1.5	0.8	2.3	-0.7	1.5	2.2	-1.3	1.9	3.3	1.9	1.7
ωB97XD/MG3S	-2.3	0.5	2.8	-1.3	0.3	1.6	-2.0	1.5	3.5	-2.1	1.5	3.7	1.9	1.8
M05-2X/MG3S	-3.3	1.5	4.8	-1.9	0.6	2.5	-0.9	1.6	2.6	-1.6	2.0	3.6	2.3	2.1
ωB97X/ma-TZVP	-0.9	2.6	3.5	-1.6	2.0	3.6	-2.7	2.6	5.2	-2.4	2.7	5.1	2.9	2.8
ωB97X/MG3S	-1.6	2.7	4.3	-1.6	1.8	3.5	-2.7	2.6	5.3	-2.4	2.7	5.2	3.0	2.9
ωB97/ma-TZVP	-0.3	4.2	4.6	-1.7	3.2	4.9	-3.4	3.5	6.8	-3.0	3.6	6.7	3.8	3.8
ωB97/MG3S	-1.1	4.2	5.4	-1.8	3.0	4.8	-3.4	3.4	6.8	-3.1	3.6	6.7	3.9	3.8

^a The values in the first line are barrier heights and energies of reaction computed by CCSD(T)-F12a/jun-cc-pVTZ, and the other lines are differences from CCSD(T)-F12a/jun-cc-pVTZ. The density functionals are listed by an order of ascending mean unsigned deviation (MUD).

^b MUD: mean unsigned deviation for four reactions of each molecule.

^c MMUD: mean MUD for the total eight reactions.

Table S2 The barrier heights (the zero point energy included, ΔE_f : forward barrier height, ΔE_r : backward barrier height) and enthalpies of reaction at 0 K (ΔH_r) of hydrogen addition reactions computed using M06-2X/ma-TZVP method for geometry optimization and energy calculation. The zero point energies (ZPEs) were calculated using scaled harmonic frequencies with a scale factor of 0.972. (in kcal/mol)

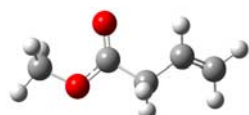
M06-2X/ma-TZVP		
	ΔH_r	-7.4
R _{1,1}	ΔE_f	13.3
	ΔE_r	20.7
R _{2,1}	ΔH_r	0.1

	ΔE_f	10.7
	ΔE_r	10.6
	ΔH_r	-33.5
R _{3,1}	ΔE_f	4.3
	ΔE_r	37.9
	ΔH_r	-36.7
R _{4,1}	ΔE_f	3.1
	ΔE_r	39.8
	ΔH_r	-19.4
R _{5,1}	ΔE_f	11.2
	ΔE_r	30.6
	ΔH_r	3.6
R _{6,1}	ΔE_f	11.9
	ΔE_r	8.3
	ΔH_r	-33.8
R _{7,1}	ΔE_f	4.1
	ΔE_r	37.9
	ΔH_r	-38.2
R _{8,1}	ΔE_f	3.8
	ΔE_r	42.0

Table S3 The geometries and Cartesian coordinates of reactants, transition states, intermediates and products of hydrogen addition reactions for methyl 3-butenate and methyl 2-butenate at the M06-2X/ma-TZVP level with integral grid of 99974 (coordinate units: Angstrom)

Reactants

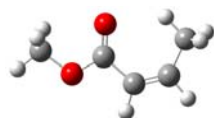
Methyl 3-butenate



Coordinates

C	0.79398300	-0.59662900	0.44161700
C	2.00924600	0.24475000	0.21128200
H	0.82932500	-1.52666600	-0.12555300
H	0.71765300	-0.87879200	1.49798400
C	3.07548000	-0.17027900	-0.45304300
H	1.97685400	1.24659000	0.62469000
H	3.93882400	0.46750900	-0.58762700
H	3.12208100	-1.16262800	-0.88728700
C	-0.48827700	0.13411000	0.11894300
O	-0.60310900	1.32234800	0.00495500
O	-1.51474700	-0.71954000	0.00327000
C	-2.78178300	-0.11764600	-0.25648100
H	-2.75069300	0.43973300	-1.19138600
H	-3.05076700	0.56171500	0.55105000
H	-3.49232700	-0.93576100	-0.32158200

Methyl 2-butenoate



Coordinates

C	1.99061800	0.68607300	-0.00011400
C	0.69346000	0.98854600	0.00005300
H	0.38121300	2.02420900	0.00000400
C	-0.41392500	0.00761700	0.00033800
O	-0.33037700	-1.19339100	0.00011200
O	-1.59702000	0.64766900	0.00002000
C	-2.74397900	-0.19606100	-0.00016800
H	-3.60295900	0.46801100	-0.00040700
H	-2.74907600	-0.82995500	0.88563300
H	-2.74869100	-0.83009200	-0.88587200
H	2.67682000	1.52897500	-0.00027900
C	2.63664600	-0.65817900	-0.00008900
H	3.28497100	-0.74839000	-0.87515100
H	1.91474500	-1.46673800	0.00009000
H	3.28522900	-0.74823100	0.87479900

Transition state

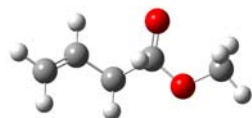
TS_{1,1}



Coordinates

C	-0.84981100	-0.60652000	0.90541300
C	-1.72435800	-0.63186400	-0.32350000
H	-1.31792400	-0.02390900	1.69669700
H	-0.62585600	-1.61047500	1.26099100
C	-2.57833900	0.33653600	-0.62111100
H	-1.55367200	-1.44452600	-1.02120600
H	-3.14114900	0.32789100	-1.54528000
H	-2.74586000	1.16707000	0.05492700
C	0.41156700	0.09358000	0.49334100
O	0.51368400	1.32317300	0.44350700
O	1.32339000	-0.71948100	-0.04694000
C	2.48436000	-0.08696200	-0.58558300
H	3.00501400	0.46887100	0.19371000
H	2.20807000	0.59489900	-1.38765900
H	3.10913500	-0.88944800	-0.96497900
H	-0.09486700	1.95147500	-0.67109200

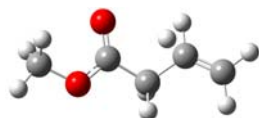
TS_{2,1}



Coordinates

C	-0.80790800	-0.51659700	-0.55728200
C	-2.02622600	0.26854000	-0.19117700
H	-0.85517200	-1.53820700	-0.18371600
H	-0.69274400	-0.56516500	-1.64601600
C	-3.06638100	-0.24520300	0.44607200
H	-2.01454300	1.31721300	-0.46755600
H	-3.92964200	0.35766000	0.69456000
H	-3.09082700	-1.28861000	0.73982700
C	0.47270100	0.14564600	-0.06158900
O	0.65126300	1.35990000	-0.05945400
O	1.49934700	-0.73914300	-0.06278000
C	2.76815100	-0.18232400	0.25669100
H	2.73569800	0.28388500	1.24343900
H	3.05519400	0.56905200	-0.47743200
H	3.46983000	-1.01088900	0.25329000
H	0.07529700	0.08862400	1.46517900

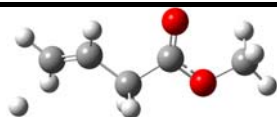
TS_{3,1}



Coordinates

C	-0.78016300	-0.52221400	0.47878100
C	-1.95268400	0.28594400	-0.00415700
H	-0.82966500	-0.61185300	1.56990300
H	-0.78671400	-1.53143700	0.07116000
C	-3.15226000	-0.25024400	-0.26262100
H	-1.83588600	1.36238600	0.06060900
H	-3.99814500	0.37117800	-0.52199800
H	-3.30405500	-1.32298200	-0.26446400
C	0.54004600	0.14661300	0.18318700
O	0.72064700	1.33285600	0.17970700
O	1.50962700	-0.74828300	-0.03666400
C	2.80357300	-0.19647500	-0.27735600
H	3.12964700	0.39018600	0.58018500
H	2.78084900	0.44457700	-1.15712400
H	3.46334300	-1.04361800	-0.43632200
H	-1.21264100	0.48324400	-1.75330900

TS_{4,1}



Coordinates

C	-0.73879200	-0.57223800	0.34390900
C	-1.92207000	0.31352400	0.13546000
H	-0.70524800	-0.92027800	1.38404300
H	-0.78251800	-1.46729600	-0.27655900
C	-3.03876900	-0.08314100	-0.47917000
H	-1.85186000	1.31096900	0.55329200
H	-3.86745700	0.59563400	-0.62876200
H	-3.10211600	-1.05043400	-0.96400900
C	0.57302500	0.13827300	0.10519600
O	0.72141600	1.32728100	0.05799500
O	1.57912400	-0.73653200	-0.01992900
C	2.87071800	-0.15859100	-0.20416200
H	3.12817100	0.47074400	0.64644500
H	2.88800600	0.44602800	-1.10956300
H	3.56071900	-0.99247600	-0.28678000
H	-4.13668500	-0.94584400	0.96997000

TS_{4,2}



Coordinates

C	-1.283616	-0.983607	-0.756255
C	-1.812897	-0.584553	0.418008
H	-0.830194	-1.960760	-0.858537
H	-1.513637	-0.449690	-1.670506
C	-2.512147	0.717573	0.612247
H	-1.650051	-1.196328	1.299806
H	-1.922932	1.378430	1.255530
H	-2.666414	1.226956	-0.338344
C	0.692135	0.073893	-0.656278
O	0.737139	1.250579	-0.796030
O	1.494262	-0.688406	0.069559
C	2.549326	0.011639	0.756772
H	2.121631	0.745072	1.438530
H	3.191261	0.515844	0.036728
H	3.102058	-0.746801	1.301556
H	-3.479737	0.580217	1.100034

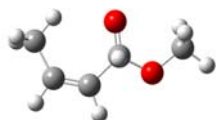
TS_{5,1}



Coordinates

C	1.98638700	-0.70994100	0.04242600
C	0.68611000	-1.02366100	0.03073400
H	0.38761500	-2.06046700	0.11194600
C	-0.41638400	-0.07719400	-0.04775000
O	-0.31666600	1.15584000	-0.06415500
O	-1.61258300	-0.67651200	0.02315700
C	-2.74643700	0.18356100	-0.04201000
H	-3.61407900	-0.46691900	0.00842500
H	-2.74208700	0.74475300	-0.97625200
H	-2.74470500	0.88286800	0.79224500
H	2.67031600	-1.54844100	0.14094000
C	2.64455300	0.62361200	-0.08569000
H	3.15195900	0.87456500	0.84896700
H	1.94731100	1.41853100	-0.32577600
H	3.41925700	0.56938200	-0.85417400
H	0.03303900	1.77284200	1.19540300

TS_{6,1}



Coordinates

C	2.00213800	0.68668400	-0.05258600
C	0.71144300	0.99140400	0.06885000
H	0.39329200	2.02431000	0.11698000
C	-0.41663600	0.00998900	0.14182200
O	-0.32213100	-1.21552800	0.09843100
O	-1.58947000	0.64647400	-0.13554600
C	-2.73419700	-0.19296200	-0.13029700
H	-3.58455900	0.45614300	-0.31710100
H	-2.83768000	-0.68369900	0.84009200
H	-2.65767300	-0.95730300	-0.90220100
H	2.68422900	1.53071100	-0.10817900
C	2.64030600	-0.65969600	-0.12545400
H	3.29352300	-0.70889800	-0.99911300
H	1.91158200	-1.46174700	-0.16645000
H	3.28008900	-0.80721100	0.74900200
H	-0.40832000	0.14762500	1.66987800

TS_{7,1}



Coordinates

C	-1.99079400	0.65845300	-0.12477200
C	-0.69462300	1.00760300	-0.02095800
H	-0.39441500	2.03937200	-0.14352500
C	0.40743000	0.01561700	0.01028300

O	0.28388400	-1.17649400	0.11394200
O	1.59791600	0.62335300	-0.09995700
C	2.72786200	-0.24329100	-0.05828600
H	3.59883900	0.39813000	-0.15011700
H	2.68882700	-0.95780500	-0.87932200
H	2.75013300	-0.78904800	0.88407300
H	-2.70098600	1.47165000	-0.22907100
C	-2.54878600	-0.72359800	-0.04561900
H	-2.36728900	-1.14742000	0.94543700
H	-2.05379100	-1.39293800	-0.74874400
H	-3.61966600	-0.72064400	-0.23562100
H	-0.36259200	1.23512100	1.88112900

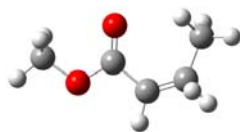
TS_{7,2}



Coordinates

C	1.81318200	0.58446600	0.41818500
C	1.28352500	0.98405800	-0.75570700
H	0.82995100	1.96120700	-0.85739500
C	-0.69214200	-0.07376700	-0.65608100
O	-0.73689100	-1.25045200	-0.79590300
O	-1.49463500	0.68834600	0.06953500
C	-2.54971000	-0.01194300	0.75649200
H	-3.10296600	0.74641500	1.30085800
H	-2.12200100	-0.74502900	1.43861500
H	-3.19114300	-0.51658700	0.03630900
H	1.65050100	1.19581400	1.30031100
C	2.51252100	-0.71772600	0.61169900
H	2.66697800	-1.22649700	-0.33918400
H	1.92324400	-1.37904500	1.25445600
H	3.48001300	-0.58060300	1.09973800
H	1.51337700	0.45064000	-1.67029300

TS_{8,1}

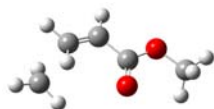


Coordinates

C	-1.96016500	0.64575800	-0.07982100
C	-0.65968000	0.98621400	-0.12783300
H	-0.37148300	2.02511500	-0.21130900
C	0.44597600	0.01806300	-0.03712100
O	0.34744200	-1.18211100	0.01180700
O	1.63229800	0.65098800	-0.02222300
C	2.77208900	-0.19895000	0.05464400
H	3.63575900	0.45886800	0.05088600
H	2.80007500	-0.87446100	-0.79943300
H	2.74398500	-0.78993100	0.96918500

H	-2.67063400	1.45308900	-0.22902200
C	-2.53201000	-0.73945500	-0.04060700
H	-3.57056900	-0.71022400	0.28407100
H	-1.95920300	-1.39529000	0.60841900
H	-2.49842000	-1.17402300	-1.04294900
H	-2.34469300	0.98606500	1.83790300

TS_{8,2}

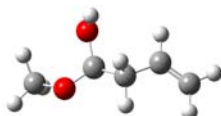


Coordinates

C	-1.79006800	0.74466000	0.60163800
C	-0.61783700	0.99493000	-0.01505100
H	-0.48444500	1.81520100	-0.70644600
C	0.51889500	0.08883600	0.19356400
O	0.49102400	-0.92866700	0.84130500
O	1.62292800	0.52102300	-0.44086500
C	2.77245300	-0.30433300	-0.28693300
H	3.56524300	0.17901000	-0.84981000
H	2.57876800	-1.30269600	-0.67736500
H	3.04375100	-0.38570900	0.76488800
H	-2.61480000	1.44004700	0.52911500
C	-2.91651400	-0.80938900	-0.70467600
H	-3.82243900	-0.89493800	-0.12245400
H	-2.17990000	-1.59235400	-0.60931300
H	-2.97095500	-0.27791700	-1.64213800
H	-1.82841800	-0.00771200	1.37875200

Intermediates

Int1

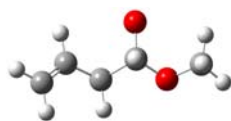


Coordinates

C	0.82304100	-0.31877800	0.62383200
C	2.03106700	0.26912200	-0.04465700
H	0.87943500	-1.40643900	0.63806800
H	0.78858600	0.01444000	1.67682200
C	3.09198300	-0.43070900	-0.41280900
H	2.00362600	1.33912900	-0.22805900
H	3.94183400	0.04006100	-0.88896900
H	3.14521200	-1.50157500	-0.25275000
C	-0.45231500	0.09168100	-0.03772300
O	-0.74112600	1.42966500	-0.05601400
O	-1.49146100	-0.73074200	0.25291400
C	-2.71354900	-0.42087800	-0.39873200
H	-2.56485600	-0.38154800	-1.48010200
H	-3.10850900	0.53542900	-0.05713700

H	-3.40576600	-1.22019300	-0.14830900
H	-0.50023100	1.84669500	0.78577100

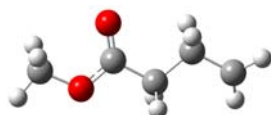
Int2



Coordinates

C	-0.79707100	-0.38477100	-0.60391500
C	-2.04827100	0.26814800	-0.11311100
H	-0.82856200	-1.46453000	-0.46271400
H	-0.63614000	-0.18620300	-1.66606500
C	-3.05866100	-0.39086500	0.43331000
H	-2.10035100	1.34658800	-0.22006000
H	-3.94984100	0.12049100	0.77246100
H	-3.03071300	-1.46801500	0.55473800
C	0.46054400	0.13020000	0.12857800
O	0.60092900	1.45462300	-0.05741900
O	1.54066100	-0.64361300	-0.29663900
C	2.75572900	-0.31142000	0.34172100
H	2.67217600	-0.44094500	1.42691900
H	3.04602700	0.71857400	0.12608200
H	3.51352700	-0.99006800	-0.04145700
H	0.30753000	0.00828700	1.22305700

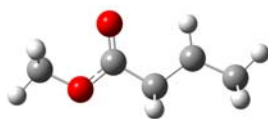
Int3



Coordinates

C	0.77137700	-0.57045700	0.02491800
C	1.94441200	0.39889900	0.00897500
H	0.80770300	-1.24739100	-0.83272100
H	0.79775900	-1.20863900	0.91140300
C	3.25424500	-0.29997200	0.00438200
H	1.84570100	1.05004600	-0.87037700
H	4.15614600	0.21932500	0.29137200
H	3.35772400	-1.27311900	-0.45548200
C	-0.56119900	0.13069700	-0.00123200
O	-0.72311700	1.31947100	-0.03765500
O	-1.57545600	-0.74663900	0.02209400
C	-2.88032000	-0.17237100	0.00091600
H	-3.57399000	-1.00716000	0.02375100
H	-3.02546400	0.47082500	0.86770100
H	-3.02010000	0.41804800	-0.90349300
H	1.87202500	1.07463800	0.86458900

Int4



Coordinates

C	-0.74042500	-0.55905300	0.00014000
C	-1.90107300	0.36257500	-0.00026300
H	-0.75251200	-1.23402400	0.86701500
H	-0.75248900	-1.23473300	-0.86616100
C	-3.27788600	-0.19035500	-0.00001200
H	-1.71429600	1.42527900	0.00016100
H	-4.02975100	0.59619400	-0.00147000
H	-3.45725700	-0.82725800	-0.87499400
C	0.59466000	0.14402500	-0.00005200
O	0.76423000	1.33107900	0.00006900
O	1.60285200	-0.74026900	-0.00010800
C	2.91058700	-0.17374500	0.00000800
H	3.05648200	0.44278700	0.88566500
H	3.05692900	0.44207400	-0.88607700
H	3.59910000	-1.01284900	0.00050400
H	-3.45803800	-0.82463100	0.87674700

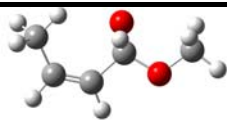
Int5



Coordinates

C	2.00677800	-0.73595200	-0.09324300
C	0.65063800	-1.02170800	-0.03464700
H	0.34618900	-2.05948600	-0.07472000
C	-0.40825000	-0.15037500	0.07654000
O	-0.34500800	1.20000000	0.08022800
O	-1.64997900	-0.62002800	0.26193700
C	-2.72585300	0.18966900	-0.19543000
H	-3.62200900	-0.40989300	-0.06394700
H	-2.59696200	0.43915400	-1.25052900
H	-2.80260100	1.10697600	0.38609700
H	2.67463300	-1.57630700	-0.21578800
C	2.63451500	0.62147600	0.00221700
H	2.32970900	1.16203800	0.90551400
H	2.41275000	1.25956000	-0.86534600
H	3.71928500	0.54119400	0.04029300
H	0.55193100	1.47833100	-0.13151200

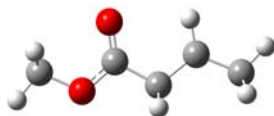
Int6



Coordinates

C	-2.00574000	-0.66816000	-0.07880100
C	-0.71599000	-0.91404800	-0.25146800
H	-0.35658300	-1.84934300	-0.66040400
C	0.39963200	0.06904200	0.07033800
O	0.31264800	1.08086300	-0.82690500
O	1.60162900	-0.63999900	0.03465800
C	2.72118800	0.15693800	0.35444900
H	3.59403100	-0.49042400	0.32784100
H	2.62060200	0.58423300	1.35899000
H	2.84743800	0.96650900	-0.36806600
H	-2.70296400	-1.45800100	-0.34110700
C	-2.60616100	0.59624100	0.44418500
H	-3.22578000	1.06248700	-0.32482500
H	-1.85145300	1.32076700	0.74207000
H	-3.25726100	0.38572400	1.29482600
H	0.26017700	0.51106400	1.07642600

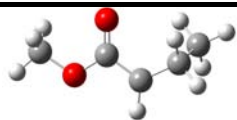
Int7



Coordinates

C	1.90107000	0.36256100	-0.00008600
C	0.74042200	-0.55906400	0.00002000
H	0.75247100	-1.23447500	-0.86650100
C	-0.59466000	0.14402300	-0.00000700
O	-0.76422700	1.33107700	0.00003600
O	-1.60285600	-0.74026800	-0.00002400
C	-2.91058800	-0.17373800	-0.00000100
H	-3.59910700	-1.01283700	-0.00002900
H	-3.05670500	0.44247100	-0.88584900
H	-3.05670200	0.44240700	0.88589400
H	1.71429100	1.42526600	-0.00010700
C	3.27789300	-0.19034500	0.00001900
H	3.45767900	-0.82607700	-0.87574400
H	3.45766200	-0.82578200	0.87600100
H	4.02973800	0.59622600	-0.00010500
H	0.75250900	-1.23430400	0.86667700

Int8

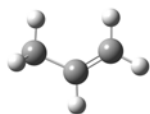


Coordinates

C	2.00273400	-0.26779800	0.54397300
C	0.68028700	-0.84971600	0.21652000
H	0.56798500	-1.88759300	-0.06392900
C	-0.49098900	-0.00035000	0.16745400
O	-0.49187200	1.18579600	0.41404500
O	-1.60283000	-0.67625300	-0.18793100
C	-2.78888000	0.10696200	-0.25201600
H	-3.58175600	-0.57456900	-0.54510800
H	-2.67950400	0.90518100	-0.98547300
H	-3.00524000	0.55127200	0.71898300
H	2.65064100	-1.03542900	0.96925100
C	2.66932700	0.33882300	-0.70246900
H	3.64157400	0.75939400	-0.44586200
H	2.04503600	1.13397600	-1.10907700
H	2.81496800	-0.41707500	-1.47479900
H	1.86903500	0.52097400	1.28633700

Products

C_3H_6



Coordinates

C	0.13442600	-0.45597500	-0.00001100
C	-1.22733700	0.16252100	-0.00000800
H	0.16985400	-1.54191300	0.00002300
H	-1.79710800	-0.15123400	0.87734800
H	-1.16519600	1.25047600	-0.00003400
H	-1.79717300	-0.15131000	-0.87723400
C	1.27235900	0.22147700	-0.00001100
H	2.23122500	-0.27993500	0.00004700
H	1.28170900	1.30577300	0.00002700

$C_2H_3O_2$

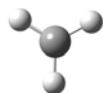


Coordinates

C	-0.81298200	0.50872200	0.00002800
O	-1.41436200	-0.50609700	0.00012200
O	0.47568100	0.73336800	-0.00007000

C	1.30864200	-0.45033000	-0.00006600
H	1.10190300	-1.03974700	-0.89107700
H	1.10235000	-1.03941900	0.89126700
H	2.33123200	-0.08935500	-0.00038400

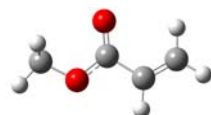
CH₃



Coordinates

C	0.00000100	0.00002400	0.00034400
H	-0.92524900	0.55167800	-0.00068700
H	0.94047400	0.52530200	-0.00068700
H	-0.01523100	-1.07712200	-0.00068700

C₄O₂H₆



Coordinates

C	2.47265400	-0.00168100	-0.00022300
C	1.31738500	-0.64764900	0.00018600
H	1.24654500	-1.72704700	0.00060700
C	0.04037900	0.11035800	0.00010800
O	-0.06125300	1.30742500	0.00018500
O	-1.01257900	-0.71949800	-0.00005300
C	-2.28752300	-0.08240900	-0.00013300
H	-3.02119400	-0.88248100	-0.00012700
H	-2.39808200	0.54115900	-0.88616400
H	-2.39815000	0.54124700	0.88582600
H	3.41671200	-0.52945400	-0.00017600
H	2.48745900	1.08144400	-0.00065800

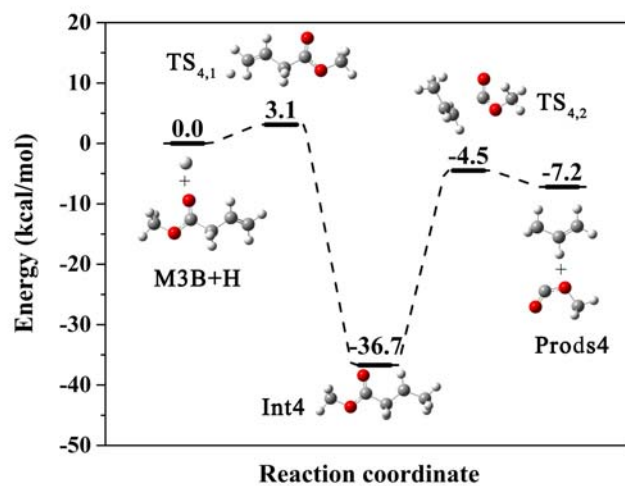


Fig. S1 The potential energy surface for hydrogen addition reaction at site 4 by M06-2X/ma-TZVP.

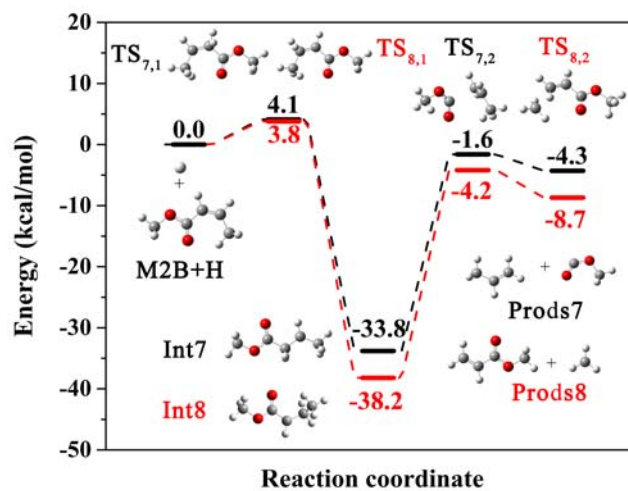


Fig. S2 The potential energy surface for hydrogen addition reaction at site 7 (in black) and 8 (in red) by M06-2X/ma-TZVP.

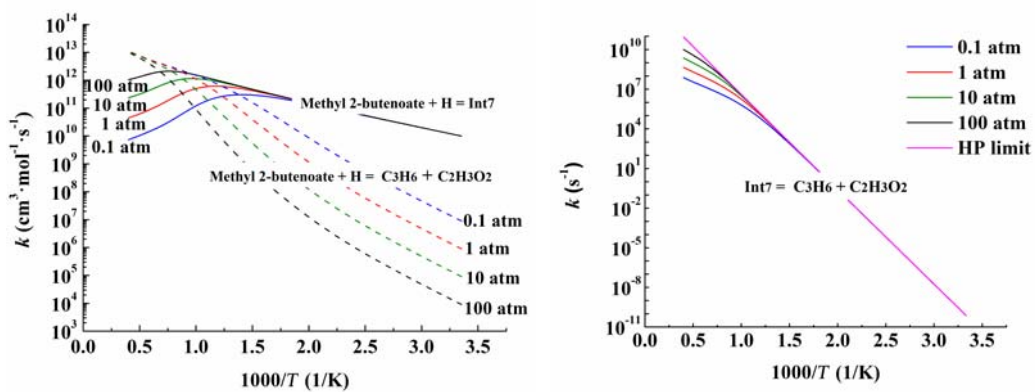


Fig. S3 Pressure-dependent rate constants of (a) $R_{7,1}$, $R_{7,3}$, and (b) $R_{7,2}$ as functions of temperature.

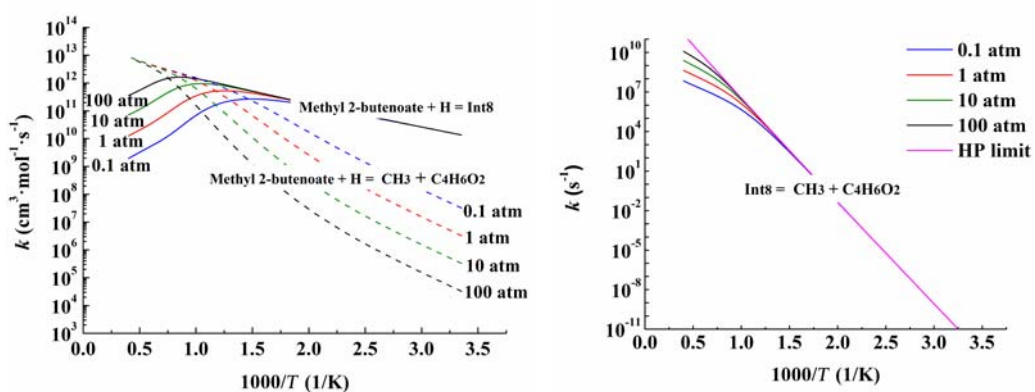


Fig. S4 Pressure-dependent rate constants of (a) $R_{8,1}$, $R_{8,3}$, and (b) $R_{8,2}$ as functions of temperature.

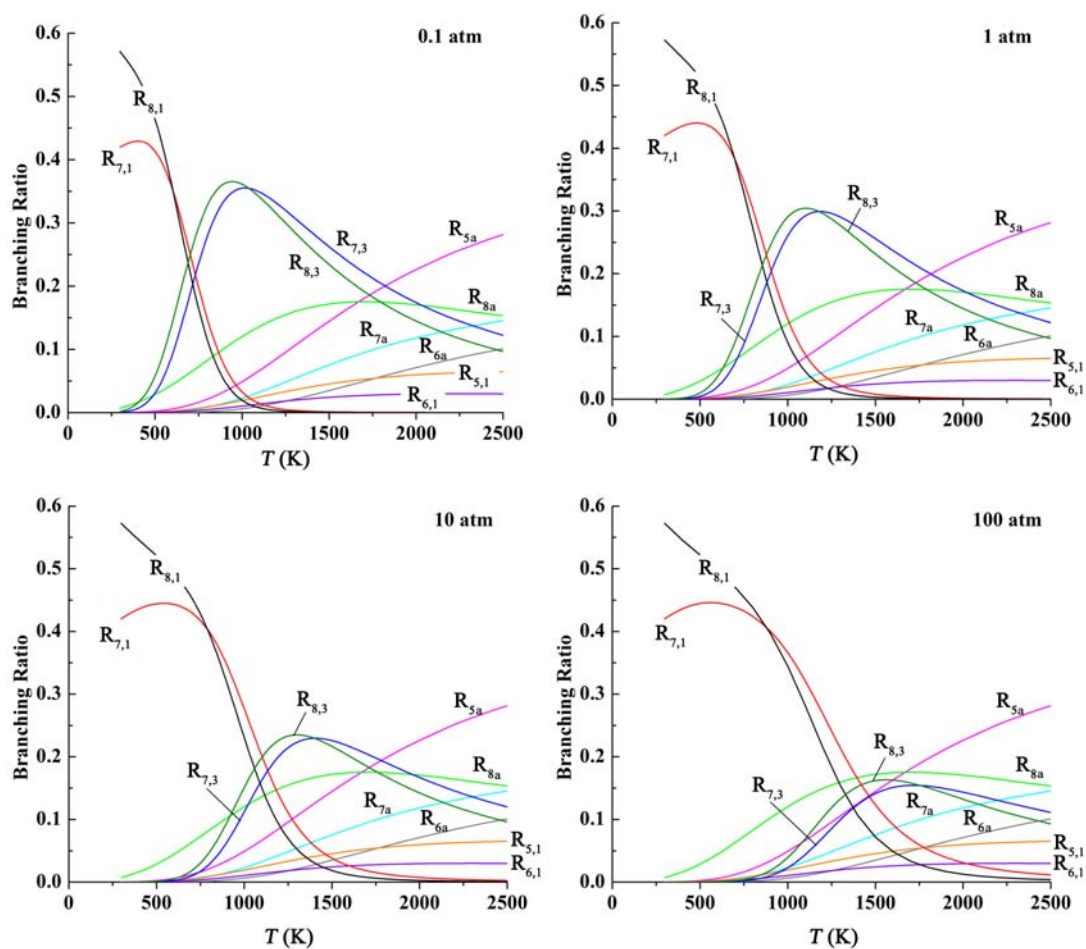
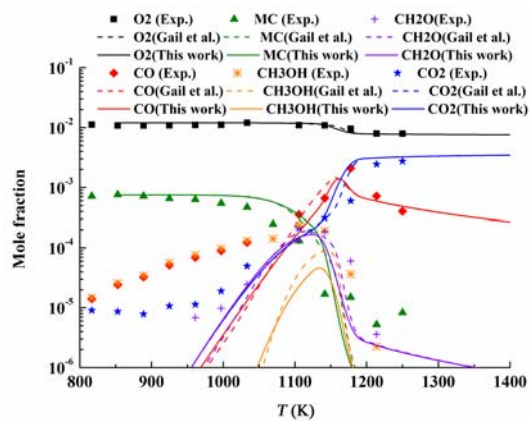
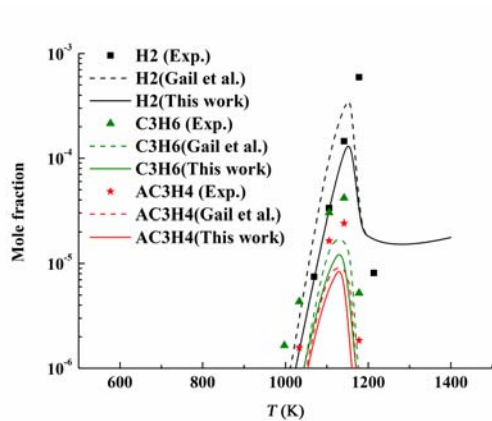


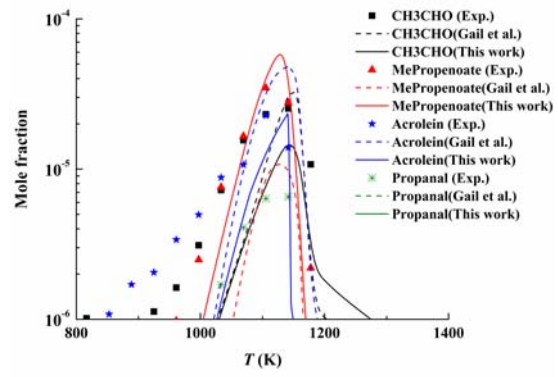
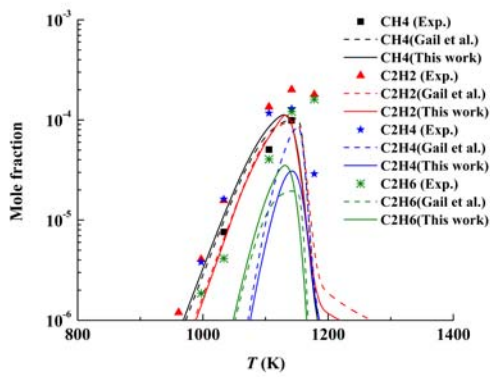
Fig. S5 Branching ratio of methyl 2-butenate + H reactions.

Table S4 The fitting parameters for the forward rate constants of hydrogen addition reactions to methyl butenoates and intermediates decomposition reactions

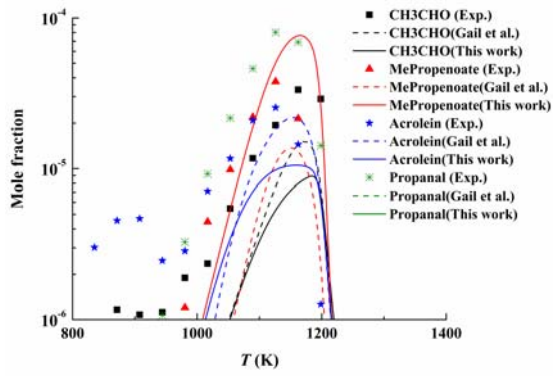
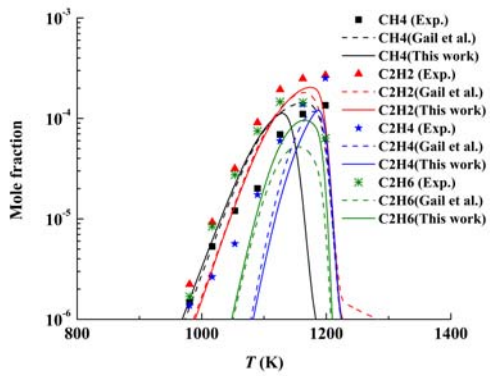
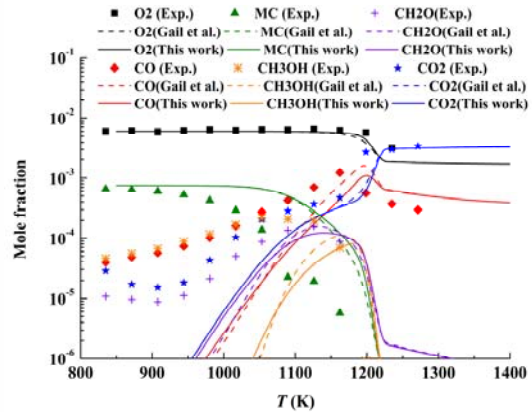
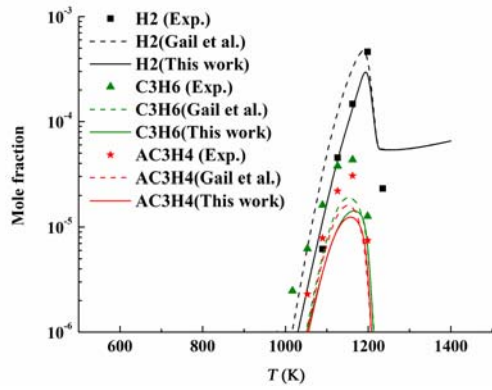
	P (atm)	B ($\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \cdot \text{K}^{-n}$)	n	E ($\text{kcal} \cdot \text{mol}^{-1}$)
$R_{1,1}$	/	$1.67\text{E}+10$	1.10	12.30
$R_{2,1}$	/	$9.54\text{E}+09$	0.95	9.91
$R_{3,1}$	/	$4.90\text{E}+09$	1.09	3.41
$R_{4,1}$	0.1	$7.48\text{E}+19$	-2.54	2.47
	1	$1.45\text{E}+20$	-2.46	3.07
	10	$3.99\text{E}+20$	-2.42	4.01
	100	$5.32\text{E}+20$	-2.27	5.37
$R_{4,3}$	0.1	$8.56\text{E}+11$	0.56	3.95
	1	$1.52\text{E}+14$	-0.04	6.43
	10	$1.57\text{E}+18$	-1.09	11.30
$R_{5,1}$	100	$1.25\text{E}+21$	-1.82	16.70
$R_{5,1}$	/	$4.42\text{E}+08$	1.47	9.95

R _{6,1}	/	2.70E+10	0.88	11.10
	0.1	1.68E+19	-2.49	2.96
R _{7,1}	1	3.93E+19	-2.43	3.56
	10	8.74E+19	-2.35	4.53
	100	1.34E+20	-2.21	6.10
	0.1	3.03E+11	0.59	4.96
R _{7,3}	1	4.54E+13	0.01	7.40
	10	6.12E+17	-1.08	12.46
	100	4.93E+20	-1.80	17.91
	0.1	1.49E+19	-2.53	2.75
R _{8,1}	1	3.45E+19	-2.48	3.24
	10	6.76E+19	-2.41	3.90
	100	9.68E+19	-2.28	4.92
	0.1	9.57E+11	0.41	4.72
R _{8,3}	1	8.61E+13	-0.12	6.83
	10	4.24E+17	-1.09	11.13
	100	4.06E+20	-1.85	15.97
<hr/>				
	<i>P</i> (atm)	<i>B</i> (s ⁻¹ ·K ^{-<i>n</i>})	<i>n</i>	<i>E</i> (kcal·mol ⁻¹)
R _{4,2}	0.1	2.92E+07	0.45	12.80
	1	5.79E+10	-0.20	16.50
	10	6.32E+14	-1.04	21.70
	100	3.06E+17	-1.52	26.40
R _{7,2}	0.1	2.66E+07	0.46	12.80
	1	3.99E+10	-0.15	16.34
	10	9.90E+14	-1.09	21.88
	100	2.68E+17	-1.51	26.41
R _{8,2}	0.1	7.75E+07	0.34	13.76
	1	9.52E+10	-0.25	17.19
	10	1.70E+15	-1.14	22.47
	100	3.97E+17	-1.53	26.65

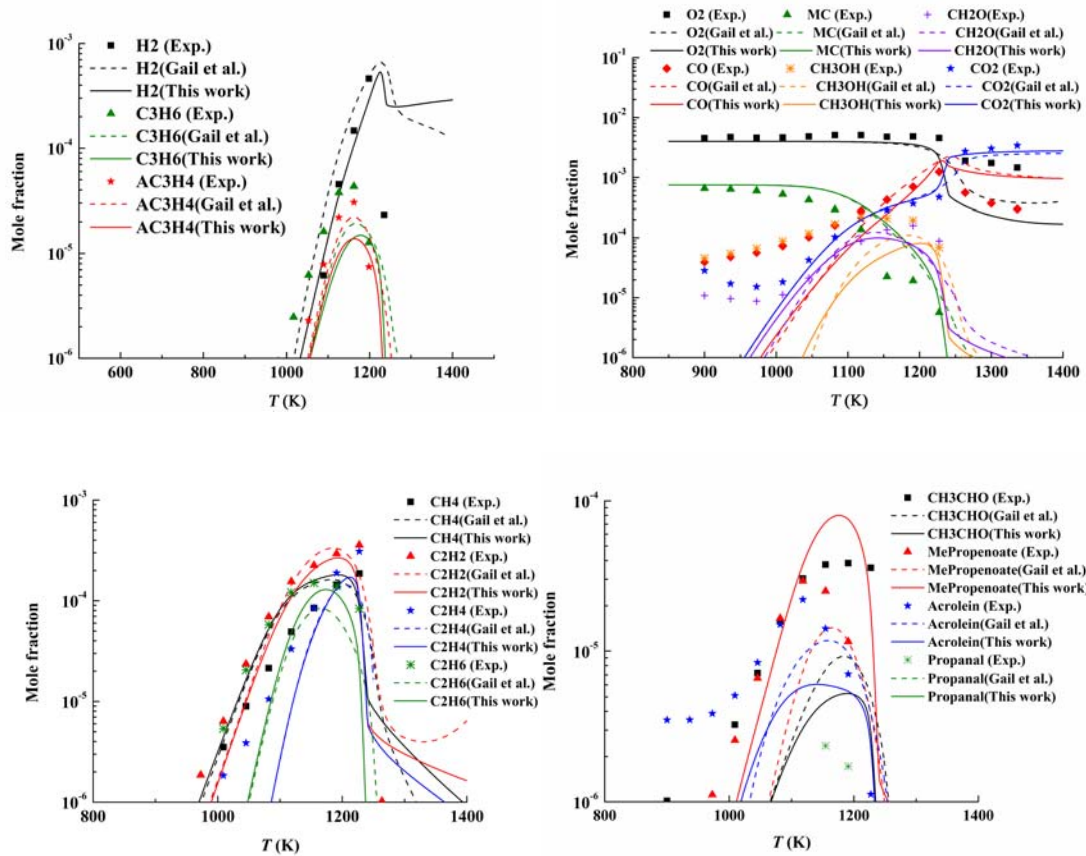




(a) JSR results and model predictions (dashed line: using the model of Gail et al.; solid line: using the model we modified) at $\Phi=0.375$.



(b) JSR results and model predictions (dashed line: using the model of Gail et al.; solid line: using the model we modified) at $\Phi=0.75$.



(c) JSR results and model predictions (dashed line: using the model of Gail et al.; solid line: using the model we modified) at $\Phi=1.13$.

Fig. S6 JSR results and model predictions using different models.