Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Contents

1. Cartesian coordinates of reactants, products and transition states for the RH+HO_2 systems at the B3LYP/def2-TZVP level of theory.

HO_2

O	0.05542200	-0.60836200	0.00000000
O	0.05542200	0.71727200	0.00000000
H	-0.88675600	-0.87127600	0.00000000

H_2O_2

O	0.00000000	0.73056900	0.00000000
H	0.95492300	0.88063300	0.00000000
O	0.00000000	-0.73056900	0.00000000
H	-0.95492300	-0.88063300	0.00000000

CH_3

C	0.00000000	0.00000000	0.00000000
H	0.00000000	1.07912500	0.00000000
H	0.93455000	-0.53956300	0.00000000
H	-0.93455000	-0.53956300	0.00000000

CH_4

C	0.00000000	0.00000000	0.00000000
H	0.62874000	0.62874000	0.62874000
H	-0.62874000	-0.62874000	0.62874000
H	-0.62874000	0.62874000	-0.62874000
H	0.62874000	-0.62874000	-0.62874000

C_2H_5

C	-0.69163500	0.00001000	-0.00204500
H	-1.09076600	-0.00151000	1.02425800
H	-1.10397600	-0.88466200	-0.49329600
H	-1.10402100	0.88607600	-0.49067500
C	0.79175600	0.00000100	-0.01801300
H	1.34904600	-0.92486100	0.04007400
H	1.34898900	0.92489200	0.03998800

C_2H_6

C	0.00000000	0.00000000	0.76346800
H	0.00000000	1.01722900	1.16103000
H	-0.88094600	-0.50861500	1.16103000
H	0.88094600	-0.50861500	1.16103000
C	0.00000000	0.00000000	-0.76346800
H	-0.88094600	0.50861500	-1.16103000

H	0.88094600	0.50861500	-1.16103000
H	0.00000000	-1.01722900	-1.16103000

n-C_3H_7

C	1.30139600	-0.29350800	-0.02677700
H	1.27712000	-1.33082400	0.28182600
H	2.26386500	0.13795200	-0.26680700
C	0.08128500	0.55060800	0.04527700
H	0.08610600	1.13092800	0.98319500
H	0.10785400	1.30733500	-0.74749700
C	-1.22552000	-0.24138500	-0.03383300
H	-1.28489600	-0.97720100	0.77162300
H	-2.09241800	0.41644800	0.05086200
H	-1.30060000	-0.77892700	-0.98120500

n-C_3H_8

C	0.00000000	1.27398600	-0.25895800
H	-0.88159200	1.31880400	-0.90393200
H	0.00000000	2.16941300	0.36633400
H	0.88159200	1.31880400	-0.90393200
C	0.00000000	0.00000000	0.58422800
H	-0.87434300	0.00000000	1.24259000
H	0.87434300	0.00000000	1.24259000
C	0.00000000	-1.27398600	-0.25895800
H	0.88159200	-1.31880400	-0.90393200
H	0.00000000	-2.16941300	0.36633400
H	-0.88159200	-1.31880400	-0.90393200

i-C_3H_7

C	-0.00942900	0.53431200	0.00000000
H	0.18960800	1.59881200	0.00000000
C	-0.00942900	-0.19700800	1.29397300
H	0.95223000	-0.70093700	1.48235200
H	-0.19241600	0.46704500	2.14008800
H	-0.76975900	-0.98640300	1.31023000
C	-0.00942900	-0.19700800	-1.29397300
H	-0.19241600	0.46704500	-2.14008800
H	0.95223000	-0.70093700	-1.48235200
H	-0.76975900	-0.98640300	-1.31023000

p-C_4H_9

C	1.88592200	-0.13295500	0.01605400
H	2.03026600	-0.84346000	-0.80188400
H	2.68268800	0.61060900	-0.04740600

H	2.01564000	-0.67938300	0.95374000
C	0.50802800	0.52049900	-0.05674600
H	0.41682500	1.08742900	-0.98806700
H	0.40300600	1.24782100	0.75489700
C	-0.64329400	-0.48689400	0.02819400
H	-0.52428300	-1.07419200	0.95531100
H	-0.54905500	-1.22411500	-0.77901600
C	-1.99380300	0.12994200	-0.00763800
H	-2.14706500	1.14959800	0.32192500
H	-2.86914200	-0.45785900	-0.24868900

s-C_4H_9

C	-1.93509600	0.16701200	-0.06272500
H	-2.01848400	0.69984900	-1.01223800
H	-2.74268000	-0.56575100	-0.01583500
H	-2.09550800	0.89094300	0.73964100
C	-0.56771500	-0.50379500	0.07091300
H	-0.44571700	-1.25865000	-0.71786000
H	-0.54331000	-1.08201600	1.01085200
C	0.57983300	0.44335600	0.03250000
H	0.39808800	1.48601800	0.26851100
C	1.98201300	-0.04248500	-0.05182200
H	2.09941800	-0.80297700	-0.83212800
H	2.68343900	0.76689500	-0.25995300
H	2.31053500	-0.51883800	0.88580800

p-C_4H_{10}

C	0.70168000	1.83100600	0.00000000
H	0.18948500	2.22523800	0.88160800
H	1.71762800	2.23153500	0.00000000
H	0.18948500	2.22523800	-0.88160800
C	0.70168000	0.30347700	0.00000000
H	1.25065500	-0.06187800	0.87486700
H	1.25065500	-0.06187800	-0.87486700
C	-0.70168000	-0.30347700	0.00000000
H	-1.25065500	0.06187800	-0.87486700
H	-1.25065500	0.06187800	0.87486700
C	-0.70168000	-1.83100600	0.00000000
H	-0.18948500	-2.22523800	0.88160800
H	-1.71762800	-2.23153500	0.00000000
H	-0.18948500	-2.22523800	-0.88160800

i-C_4H_9

C	-1.26843500	-0.67952600	0.10135900

H	-2.16742100	-0.16524800	-0.24477000
H	-1.28901100	-1.69649000	-0.29605800
H	-1.31588900	-0.74121800	1.19135100
C	0.00003500	0.05972100	-0.34545900
H	0.00004800	0.05296400	-1.45014300
C	-0.00036600	1.48021100	0.10114400
H	0.92598100	2.03149600	0.19905300
H	-0.92702600	2.03091300	0.19928500
C	1.26874400	-0.67898200	0.10139700
H	1.28985500	-1.69583200	-0.29628200
H	2.16755500	-0.16420700	-0.24445500
H	1.31603700	-0.74091700	1.19137400

t-C_4H_9

C	0.00000000	1.48206500	-0.01471200
H	-0.88571200	1.94041200	0.43273100
H	0.88571200	1.94041200	0.43273100
H	0.00000000	1.77662900	-1.07823500
C	0.00000000	0.00000000	0.15052200
C	1.28350600	-0.74103300	-0.01471200
H	2.12330200	-0.20315700	0.43273100
H	1.23759000	-1.73725500	0.43273100
H	1.53860600	-0.88831400	-1.07823500
C	-1.28350600	-0.74103300	-0.01471200
H	-1.23759000	-1.73725500	0.43273100
H	-2.12330200	-0.20315700	0.43273100
H	-1.53860600	-0.88831400	-1.07823500

i-C_4H_{10}

C	0.00000000	1.45821400	-0.09535400
H	0.88286800	1.99110500	0.26538800
H	0.00000000	1.51728100	-1.18789400
H	-0.88286800	1.99110500	0.26538800
C	0.00000000	0.00000000	0.37015700
H	0.00000000	0.00000000	1.46678200
C	1.26285000	-0.72910700	-0.09535400
H	2.16578100	-0.23096700	0.26538800
H	1.28291400	-1.76013800	0.26538800
H	1.31400400	-0.75864000	-1.18789400
C	-1.26285000	-0.72910700	-0.09535400
H	-1.28291400	-1.76013800	0.26538800
H	-2.16578100	-0.23096700	0.26538800
H	-1.31400400	-0.75864000	-1.18789400

TS1

C	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.08420300
H	0.97686500	0.00000000	-0.47011200
H	-0.75321000	-0.62092600	-0.47218500
H	-0.51967100	1.29788500	-0.29975700
O	-0.92764200	2.31825300	-0.53227100
O	-1.56296700	2.18178200	-1.78773700
H	-0.89683000	2.53478699	-2.39742500

TS2

O	1.69844100	-0.64031900	0.12105500
H	2.12750400	-0.41205800	0.96000400
O	1.26526800	0.61922800	-0.35225100
H	0.14654700	0.67808200	-0.06462300
C	-1.19986400	0.70016600	0.26838400
H	-1.15501000	0.88975100	1.33893400
H	-1.53275700	1.56420200	-0.30290800
C	-1.73792400	-0.63332100	-0.15252600
H	-2.79742000	-0.72605200	0.12066800
H	-1.66593000	-0.77364000	-1.23186400
H	-1.20586700	-1.45262500	0.33421100

TS3

O	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.41424700
H	0.94668100	0.00000000	1.62345400
H	-0.15631200	-1.10856400	-0.29750600
C	-0.36871600	-2.44652500	-0.59744500
H	0.60206900	-2.87337599	-0.35279700
H	-0.55336100	-2.39078000	-1.66945700
C	-1.52337700	-2.87418100	0.26035500
H	-1.61733900	-3.96867900	0.19049800
H	-1.29243000	-2.66849100	1.31028400
C	-2.85222400	-2.22364000	-0.12047100
H	-3.66021800	-2.57874300	0.52116300
H	-2.79574000	-1.13838799	-0.02301300
H	-3.12013500	-2.45456300	-1.15438900

TS4

O	-1.52498300	-0.32545600	0.68315900
O	-2.00186900	0.01944600	-0.60107300
H	-2.30171200	0.93282100	-0.47526600
H	-0.35140300	-0.18531000	0.61978300

C	0.98897200	-0.00911900	0.48838300
H	1.28260500	-0.07096300	1.53757300
C	1.43329600	-1.17844200	-0.34682700
H	2.51781400	-1.14168500	-0.51508700
H	1.20736000	-2.12941000	0.13677000
H	0.95177800	-1.17012900	-1.32719500
C	1.13588200	1.36253800	-0.11072900
H	0.72756900	2.13665500	0.54106300
H	2.19463800	1.60037600	-0.27810000
H	0.63726600	1.42586800	-1.08119600

TS5

O	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.41416700
H	0.94663100	0.00000000	1.62358300
H	-0.15900800	-1.10943800	-0.29734300
C	-0.37698100	-2.44675100	-0.59251700
H	0.60721100	-2.86806900	-0.39709600
H	-0.61317800	-2.38836100	-1.65414800
C	-1.48526300	-2.88591100	0.31827800
H	-1.57577900	-3.98198500	0.25338300
H	-1.20790000	-2.67902200	1.35783300
C	-2.84165901	-2.25009300	0.00795400
H	-2.74410101	-1.16296100	0.06697800
H	-3.11527501	-2.47928500	-1.02747300
C	-3.94992800	-2.72039600	0.94661400
H	-3.71839300	-2.47124100	1.98506300
H	-4.90380301	-2.25122900	0.69892700
H	-4.08791200	-3.80331799	0.88865100

TS6

C	-1.88390100	-1.35595900	0.11068100
H	-2.48940600	-1.16945300	1.00063200
H	-1.05297900	-1.99913100	0.40724600
H	-2.50101400	-1.90700500	-0.60101800
C	-1.37943600	-0.04711900	-0.49472500
H	-0.82678500	-0.24535000	-1.42007700
H	-2.23917200	0.56831500	-0.79965900
C	-0.51647900	0.77073200	0.43106700
H	-0.89018900	0.81843400	1.45650900
C	0.02318400	2.07337100	-0.09228700
H	-0.79556000	2.77561000	-0.29718400
H	0.69345500	2.54875400	0.62452100
H	0.57027100	1.92858700	-1.02638200

H	0.59750100	0.01840200	0.62879800
O	1.58736600	-0.62688300	0.72869200
O	2.11795600	-0.67727100	-0.58018700
H	1.83109000	-1.55007500	-0.88984500

TS7

O	-2.43382600	0.05546200	-0.81525900
H	-2.92715300	-0.76861000	-0.94722300
O	-2.17485900	0.03622200	0.57529900
H	-1.09615800	-0.36650400	0.67105200
C	0.21000900	-0.83926000	0.74048500
H	0.43217300	-0.68662900	1.79651600
H	0.06729100	-1.88753300	0.48235800
C	1.00399700	-0.01399100	-0.23623500
H	0.49676400	-0.06117800	-1.20661700
C	2.40905800	-0.62188400	-0.42313200
H	2.35528600	-1.65625300	-0.76778100
H	2.97415300	-0.04804000	-1.16145000
H	2.96816600	-0.60678400	0.51558700
C	1.08734100	1.45318800	0.19107000
H	1.63736000	2.04268200	-0.54505700
H	0.09330900	1.88849800	0.29975000
H	1.60585500	1.54855900	1.14942100

TS8

C	-0.74205700	-1.11353600	-1.06318100
H	-0.53604500	-0.69499000	-2.05030800
H	-1.70996100	-1.62914000	-1.12202800
H	0.01320400	-1.87011600	-0.84091800
C	-0.78034700	-0.04133000	0.00031500
C	-1.64229900	1.15579400	-0.32730900
H	-2.70336400	0.87231700	-0.32831400
H	-1.51849900	1.95224400	0.40858600
H	-1.41177300	1.56043000	-1.31449500
C	-0.90597700	-0.55572500	1.41512100
H	-0.14110500	-1.30152700	1.63797500
H	-0.81943900	0.25148800	2.14401800
H	-1.88503600	-1.03154500	1.56143600
H	0.45915300	0.45650500	-0.02206600
O	1.58503700	0.89017700	-0.04437300
O	2.41507900	-0.23964000	0.11591500
H	2.67602000	-0.44118000	-0.79590300

2. Single point energies, correlation energies of reactants, products and transition states for the RH+HO_2 reactions with different methods.

Table S1 HF energies, CCSD-F12b and (T) correlation energies and CCSD(T)-F12b/CBS energies of for all reactants, products and transition states. (unit: Hartree.)

	HF			$\Delta E_{(CCSD-F12b)}$		$\Delta E_{(T)}$		CCSD(T)-F12b
	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z	cc-pVDZ-F12	cc-pVTZ-F12	cc-pVDZ-F12	cc-pVTZ-F12	CBS
H2O2	-150.837096	-150.847029	-150.849540	-0.544499	-0.556980	-0.020203	-0.022417	-151.435800
CH4	-40.213575	-40.216198	-40.216903	-0.228416	-0.231410	-0.006473	-0.007126	-40.457204
C2H6	-79.260216	-79.265129	-79.266365	-0.420721	-0.426338	-0.013952	-0.015217	-79.711184
n-C3H8	-118.308309	-118.315510	-118.317267	-0.614562	-0.622823	-0.021812	-0.023696	-118.968556
p-C4H10	-157.356267	-157.365757	-157.368035	-0.808601	-0.819500	-0.029744	-0.032239	-158.226043
i-C4H10	-157.356764	-157.366260	-157.368529	-0.810084	-0.821001	-0.030063	-0.032574	-158.228382
HO2	-150.232516	-150.242459	-150.244922	-0.503603	-0.515702	-0.018887	-0.020903	-150.788099
CH3	-39.573423	-39.575816	-39.576435	-0.191614	-0.194561	-0.004948	-0.005540	-39.778208
C2H5	-78.623591	-78.628315	-78.629471	-0.385742	-0.391279	-0.012612	-0.013825	-79.037739
n-C3H7	-117.671450	-117.678459	-117.680136	-0.579480	-0.587640	-0.020459	-0.022286	-118.294723
i-C3H7	-117.674872	-117.681914	-117.683599	-0.580521	-0.588661	-0.020535	-0.022369	-118.299288
p-C4H9	-156.719456	-156.728751	-156.730949	-0.773517	-0.784310	-0.028389	-0.030826	-157.552244
s-C4H9	-156.722718	-156.732041	-156.734248	-0.774410	-0.785165	-0.028443	-0.030883	-157.556445
i-C4H9	-156.719702	-156.729003	-156.731193	-0.774820	-0.785598	-0.028713	-0.031155	-157.554095
t-C4H9	-156.726589	-156.735941	-156.738148	-0.775847	-0.786589	-0.028746	-0.031191	-157.562071
TS1	-190.376913	-190.388946	-190.391973	-0.755800	-0.771403	-0.028801	-0.031690	-191.203665
TS2	-229.424055	-229.438318	-229.441859	-0.952923	-0.971146	-0.037339	-0.040808	-230.463887
TS3	-268.472099	-268.488612	-268.492660	-1.147458	-1.168315	-0.045420	-0.049488	-269.722023
TS4	-268.473249	-268.489744	-268.493793	-1.149856	-1.170711	-0.045945	-0.050001	-269.726059
TS5	-307.519998	-307.538790	-307.543355	-1.341698	-1.365189	-0.053424	-0.058092	-308.979686
TS6	-307.520852	-307.539598	-307.544154	-1.344637	-1.368129	-0.054101	-0.058757	-308.984080
TS7	-307.520468	-307.539262	-307.543819	-1.342758	-1.366266	-0.053796	-0.058466	-308.981602
TS8	-307.523010	-307.541754	-307.546305	-1.347270	-1.370749	-0.054702	-0.059348	-308.989428

Table S2 Single point energies obtained by CCSD-F12x (x=a,b), DLPNO-CC and FN-DMC methods for all reactants, products and transition states. (unit: Hartree.)

	CCSD(T)-F12b		CCSD(T)-F12a		DLPNO-CCSD(T)	DLPNO-CCSD(T1)	DLPNO-CCSD(T)-F12		FN-DMC
system	cc-pVDZ-F12	cc-pVTZ-F12	cc-pVDZ-F12	cc-pVTZ-F12	aug-cc-pVQZ		cc-pVTZ-F12	cc-pVQZ-F12	BFD-PP
H_2O_2	-151.403607	-151.427027	-151.411938	-151.434884	-151.411879	-151.412742	-151.420548	-151.429316	-33.20275(30)
CH_4	-40.449018	-40.454907	-40.453028	-40.458436	-40.451793	-40.451930	-40.453252	-40.455678	-8.09421(14)
C_2H_6	-79.695956	-79.706988	-79.702932	-79.713330	-79.700444	-79.700781	-79.703657	-79.708141	-14.98482(24)
n-C_3H_8	-118.946282	-118.962459	-118.956190	-118.971599	-118.952469	-118.953033	-118.957439	-118.963901	-21.87852(30)
p-C_4H_{10}	-158.196743	-158.218050	-158.209579	-158.229985	-158.204628	-158.205424	-158.211292	-158.219759	-28.77233(38)
i-C_4H_{10}	-158.199072	-158.220383	-158.211892	-158.232302	-158.206937	-158.207754	-158.213609	-158.222081	-28.77419(36)
HO_2	-150.757041	-150.779697	-150.764569	-150.786926	-150.764278	-150.765077	-150.774545	-150.782456	-32.55458(30)
CH_3	-39.770469	-39.776062	-39.774038	-39.779084	-39.773211	-39.773270	-39.775063	-39.777015	-7.41437(15)
C_2H_5	-79.022948	-79.033698	-79.029409	-79.039532	-79.027235	-79.027488	-79.031120	-79.035029	-14.30940(23)
n-C_3H_7	-118.272916	-118.288789	-118.282310	-118.297426	-118.278734	-118.279203	-118.284528	-118.290355	-21.20304(31)
i-C_3H_7	-118.277457	-118.293353	-118.286796	-118.301984	-118.283197	-118.283662	-118.289159	-118.294957	-21.20770(29)
p-C_4H_9	-157.523415	-157.544415	-157.535736	-157.555846	-157.530807	-157.531494	-157.538508	-157.546239	-28.09684(35)
s-C_4H_9	-157.527620	-157.548623	-157.539889	-157.560053	-157.534877	-157.535559	-157.542752	-157.550495	-157.524269
i-C_4H_9	-157.525319	-157.546280	-157.537627	-157.557704	-157.532570	-157.533274	-157.540337	-157.548065	-28.09887(37)
t-C_4H_9	-157.533261	-157.554259	-157.545456	-157.565667	-157.540405	-157.541099	-157.548391	-157.556159	-28.10692(33)
TS1	-191.163572	-191.192725	-191.175459	-191.203750	-191.173830	-191.174895	-191.185318	-191.195917	-40.60621(37)
TS2	-230.416837	-230.451081	-230.431566	-230.464924	-230.428439	-230.429734	-230.442016	-230.454515	-47.50208(42)
TS3	-269.667992	-269.707345	-269.685634	-269.723986	-269.681082	-269.682605	-269.696592	-269.710964	-54.39672(48)
TS4	-269.672048	-269.711386	-269.689621	-269.728023	-269.685004	-269.686545	-269.700556	-269.715016	-54.40080(46)
TS5	-308.918656	-308.963124	-308.939217	-308.982559	-308.933310	-308.935053	-308.950676	-308.966962	-61.29076(53)
TS6	-308.923084	-308.967529	-308.943571	-308.986963	-308.937523	-308.939290	-308.954947	-308.971332	-308.922856
TS7	-308.920581	-308.965041	-308.941127	-308.984466	-308.935113	-308.936878	-308.952533	-308.968804	-61.29180(58)
TS8	-308.928493	-308.972895	-308.948911	-308.992305	-308.942786	-308.944582	-308.960228	-308.976647	-61.30025(50)

Table S3 Single point energies obtained by those dispersion-uncorrected and dispersion-corrected DFAs for all reactants, products and transition states. (unit: Hartree.)

	dispersion-uncorrected							dispersion-corrected			
System	B3LYP	M06-2X	MN15	B2GP-PLYP	DSD-BLYP	DSD-PBEP86	DSD-PBEB95	B3LYPG	B2GP-PLYP	DSD-PBEP86	DSD-PBEB95
H_2O_2	-151.629362	-151.563372	-151.542586	-151.513731	-151.502176	-151.427296	-151.433033	-151.630700	-151.514088	-151.415778	-151.428831
CH_4	-40.542273	-40.506158	-40.494249	-40.486079	-40.480277	-40.456956	-40.453191	-40.544187	-40.486574	-40.453291	-40.452389
C_2H_6	-79.871907	-79.814215	-79.789390	-79.770864	-79.760716	-79.714740	-79.710193	-79.877321	-79.772384	-79.707644	-79.708745
n-C_3H_8	-119.203474	-119.125316	-119.087594	-119.058483	-119.044372	-118.975650	-118.970162	-119.213389	-119.061386	-118.965287	-118.968219
p-C_4H_{10}	-158.534924	-158.436428	-158.385881	-158.346100	-158.328070	-158.236603	-158.230164	-158.549507	-158.350450	-158.223004	-158.227766
i-C_4H_{10}	-158.535773	-158.438555	-158.388134	-158.347911	-158.330263	-158.238730	-158.232170	-158.551259	-158.352573	-158.225285	-158.229889
HO_2	-150.986302	-150.919985	-150.899077	-150.870073	-150.855833	-150.781677	-150.789320	-150.987169	-150.870313	-150.770610	-150.785805
CH_3	-39.862952	-39.829469	-39.817860	-39.809728	-39.803006	-39.780582	-39.776005	-39.864339	-39.810099	-39.777226	-39.775407
C_2H_5	-79.200038	-79.143988	-79.120204	-79.100628	-79.089365	-79.044182	-79.039127	-79.204674	-79.101969	-79.037297	-79.037874
n-C_3H_7	-118.531347	-118.454723	-118.418012	-118.387847	-118.372559	-118.304647	-118.298686	-118.540364	-118.390539	-118.294496	-118.296933
i-C_3H_7	-118.537628	-118.459998	-118.423881	-118.393001	-118.377530	-118.309541	-118.303819	-118.546431	-118.395647	-118.299305	-118.302066
p-C_4H_9	-157.862840	-157.765936	-157.716393	-157.675502	-157.656292	-157.565641	-157.558727	-157.876528	-157.679641	-157.552252	-157.556518
s-C_4H_9	-157.868862	-157.770828	-157.721798	-157.680288	-157.660839	-157.570125	-157.563473	-157.882214	-157.684351	-157.556650	-157.561258
i-C_4H_9	-157.863298	-157.767583	-157.717978	-157.676795	-157.657896	-157.567196	-157.560181	-157.877741	-157.681209	-157.553963	-157.558085
t-C_4H_9	-157.874706	-157.776685	-157.728139	-157.685979	-157.666672	-157.575852	-157.569335	-157.888655	-157.690284	-157.562459	-157.567247
TS1	-191.488701	-191.385226	-191.350694	-191.314156	-191.295675	-191.198376	-191.199530	-191.493522	-191.315508	-191.183803	-191.195261
TS2	-230.825017	-230.699988	-230.652622	-230.605231	-230.582490	-230.462346	-230.462847	-230.834010	-230.607845	-230.444401	-230.458053
TS3	-270.156657	-270.011754	-269.951507	-269.893288	-269.866698	-269.723796	-269.723370	-270.170628	-269.897448	-269.702681	-269.718189
TS4	-270.161412	-270.016055	-269.955809	-269.897601	-269.870989	-269.727972	-269.727587	-270.175557	-269.901824	-269.706842	-269.722425
TS5	-309.488139	-309.322985	-309.249934	-309.181012	-309.150527	-308.984866	-308.983497	-309.506916	-309.186672	-308.960548	-308.977900
TS6	-309.492611	-309.327618	-309.254633	-309.185370	-309.154964	-308.989198	-308.987859	-309.511964	-309.191223	-308.964944	-308.982365
TS7	-309.488427	-309.324536	-309.251470	-309.182336	-309.152216	-308.986488	-308.984983	-309.507982	-309.188271	-308.962307	-308.979477
TS8	-309.497421	-309.332727	-309.259629	-309.190665	-309.160541	-308.994582	-308.993163	-309.517502	-309.196785	-308.970414	-308.987742

3. Deviations of the barrier heights, reaction energies and X-H bond energies for DFA-D3(BJ) with respect to the CCSD(T)-F12b/CBS values and differences between barrier heights of R1-R8 reactions by those dispersion-corrected and dispersion-uncorrected DFAs. .

Table S4 Deviations of the barrier heights for DFA-D3(BJ) with respect to the CCSD(T)-F12b/CBS values. (unit: kJ/mol)

Reaction	Barrier	B3LYP	B2GP-PLYP	DSD-PBEP86	DSD-PBEB95
R1	$V_f^{\neq}$	-10.00	-0.67	-4.06	3.39
	$V_r^{\neq}$	-23.18	-4.35	-3.01	-3.60
R2	$V_f^{\neq}$	-12.89	-1.42	-4.06	2.89
	$V_r^{\neq}$	-21.76	-3.81	-2.59	-2.64
R3	$V_f^{\neq}$	-12.34	-1.00	-3.72	3.18
	$V_r^{\neq}$	-21.17	-3.47	-2.38	-2.43
R4	$V_f^{\neq}$	-14.69	-1.88	-4.06	2.64
	$V_r^{\neq}$	-19.58	-2.97	-2.09	-1.46
R5	$V_f^{\neq}$	-12.34	-0.96	-3.64	3.18
	$V_r^{\neq}$	-21.09	-3.39	-2.26	-2.38
R6	$V_f^{\neq}$	-14.02	-1.34	-3.64	3.01
	$V_r^{\neq}$	-18.91	-2.47	-1.76	-1.13
R7	$V_f^{\neq}$	-11.63	-0.71	-3.39	3.51
	$V_r^{\neq}$	-20.54	-3.31	-2.26	-2.22
R8	$V_f^{\neq}$	-16.11	-2.51	-4.14	2.34
	$V_r^{\neq}$	-17.32	-2.26	-1.63	-0.29
MD		-16.72	-2.28	-3.04	0.50
MAD		16.72	2.28	3.04	2.52

Table S5 Differences between barrier heights of R1-R8 reactions by those dispersion-corrected and dispersion-uncorrected DFAs. (unit: kJ/mol)

Reaction	Barrier	B3LYP	B2GP-PLYP	DSD-PBEP86	DSD-PBEB95
R1	$V_f^{\neq}$	-5.36	-1.59	-0.42	-0.12
	$V_r^{\neq}$	-5.52	-1.63	-0.79	-1.42
R2	$V_f^{\neq}$	-7.12	-2.26	-0.59	-0.46
	$V_r^{\neq}$	-7.91	-2.43	-1.21	-1.72
R3	$V_f^{\neq}$	-8.37	-2.67	-0.83	-0.71
	$V_r^{\neq}$	-9.50	-2.93	-1.46	-2.05
R4	$V_f^{\neq}$	-8.83	-2.80	-0.80	-0.75
	$V_r^{\neq}$	-10.50	-3.22	-1.63	-2.05
R5	$V_f^{\neq}$	-8.74	-2.80	-0.92	-0.84
	$V_r^{\neq}$	-9.84	-3.06	-1.51	-2.17
R6	$V_f^{\neq}$	-10.25	-3.31	-1.09	-1.13
	$V_r^{\neq}$	-12.22	-3.77	-1.93	-2.43
R7	$V_f^{\neq}$	-8.37	-2.72	-0.84	-0.76
	$V_r^{\neq}$	-9.91	-3.06	-1.51	-2.09
R8	$V_f^{\neq}$	-9.79	-3.18	-0.92	-1.01
	$V_r^{\neq}$	-12.59	-3.85	-1.96	-2.30

Table S6 Deviations of the reaction energies for DFA-D3(BJ) with respect to the CCSD(T)-F12b/CBS results. (unit: kJ/mol)

Reaction	B3LYP	B2GP-PLYP	DSD-PBEP86	DSD-PBEB95
R1	13.18	3.68	-1.05	6.99
R2	8.87	2.38	-1.46	5.52
R3	8.83	2.47	-1.34	5.61
R4	4.90	1.09	-1.97	4.10
R5	8.74	2.43	-1.38	5.56
R6	4.90	1.13	-1.88	4.14
R7	8.91	2.59	-1.13	5.73
R8	1.21	-0.25	-2.51	2.64
MAD	7.44	2.00	1.59	5.04

Table S7 Deviations of the X-H bond energies for DFA-D3(BJ) with respect to the CCSD(T)-F12b/CBS results. (unit: kJ/mol)

Dissociation system	B3LYP	B2GP-PLYP	DSD-PBEP86	DSD-PBEB95
1.H_2O_2→HO_2+H	-17.25	-7.91	-4.22	-6.59
2. CH_4→CH_3+H	-4.08	-4.23	-5.28	0.38
3.C_2H_6→C_2H_5+H	-8.42	-5.58	-5.74	-1.10
4.n-C_3H_8→n-C_3H_7+H	-8.43	-5.45	-5.57	-1.02
5.n-C_3H_8→i-C_3H_7+H	-12.39	-6.89	-6.23	-2.52
6.p-C_4H_{10}→p-C_4H_9+H	-8.47	-5.47	-5.59	-1.04
7.p-C_4H_{10}→s-C_4H_9+H	-12.35	-6.79	-6.09	-2.43
8.i-C_4H_{10}→i-C_4H_9+H	-8.35	-5.30	-5.39	-0.87
9.i-C_4H_{10}→t-C_4H_9+H	-16.04	-8.17	-6.73	-3.96
MAD	10.64	6.20	5.65	2.21