Mechanistic insights into H_2 evolution from water splitting at the expense of $B_2(OH)_4$: A theoretical study

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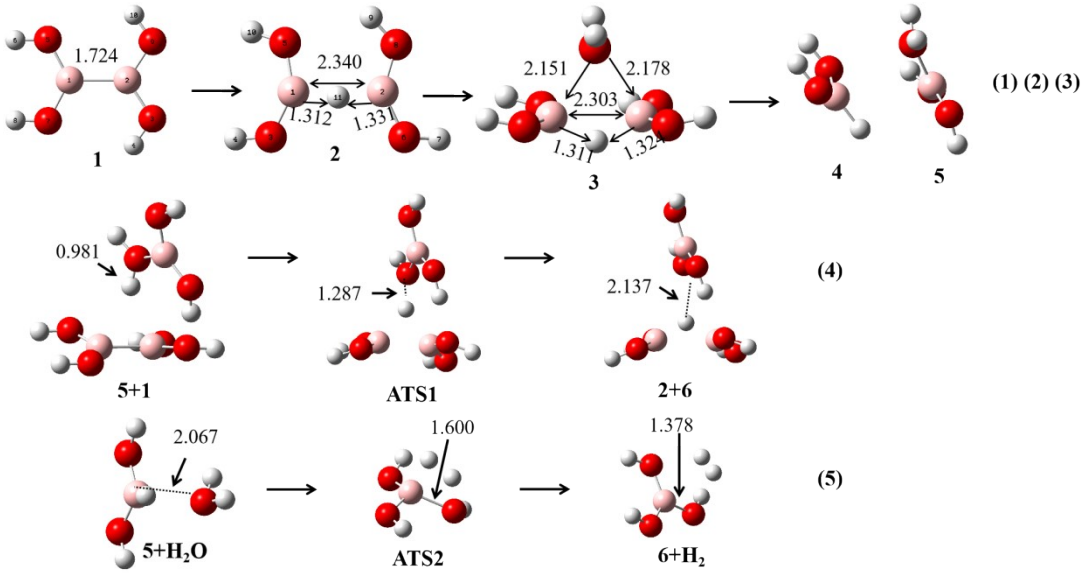
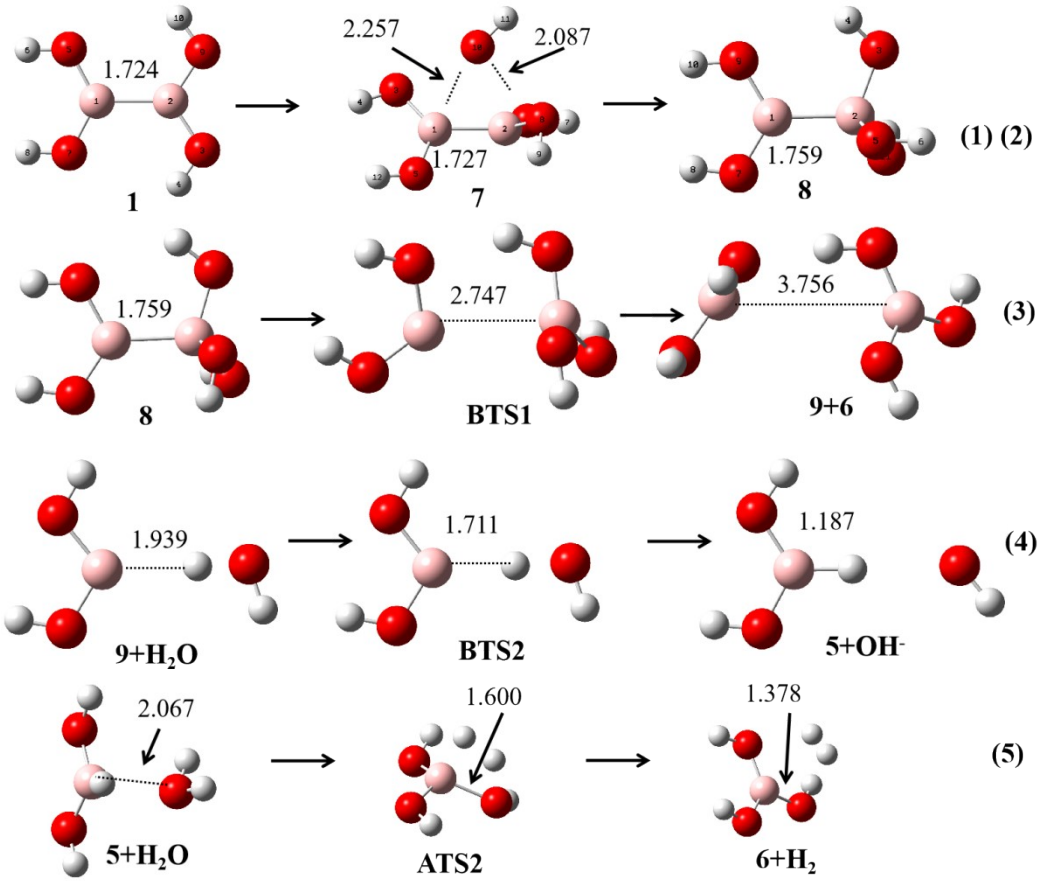


Scheme S1. Schematic diagram illustrating the formation of hydrogen and $B(OH)_3$ from tetrahydroxy diboron with water in the presenceof acid, chemical structural formulas are replaced by optimized geometries. The typical distances in water are given in Å.

Table S1 Single point energy (SPE/hartree), ΔE and ΔG (kcal/mol) for formation of hydrogen from tetrahydroxy diboron with water at the presence of acid.

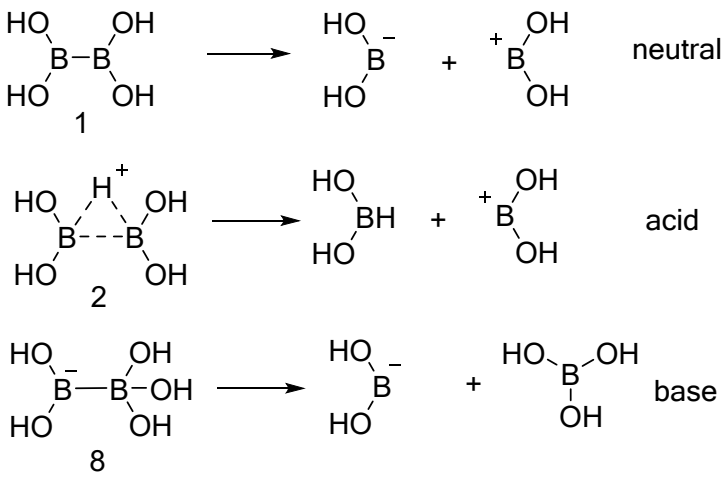
Step 1	$1+H^+$	2		ΔE	ΔG
	-353.5601575	-353.7804678			-138.2
Step 2	$2+H_2O$	3			
	-430.2466499	-430.2672742			-12.9
Step 3	3	4+5			
	-430.2672742	-430.3004768			-20.9
Step 4	1+4	ATS1	2+6		
	-606.4050427	-606.3856684	-606.4088494	12.2	-2.4
Step 5	$5+H_2O$	ATS2	$6+H_2$		
	-253.7663068	-253.7155015	-253.8012791	31.9	-21.9



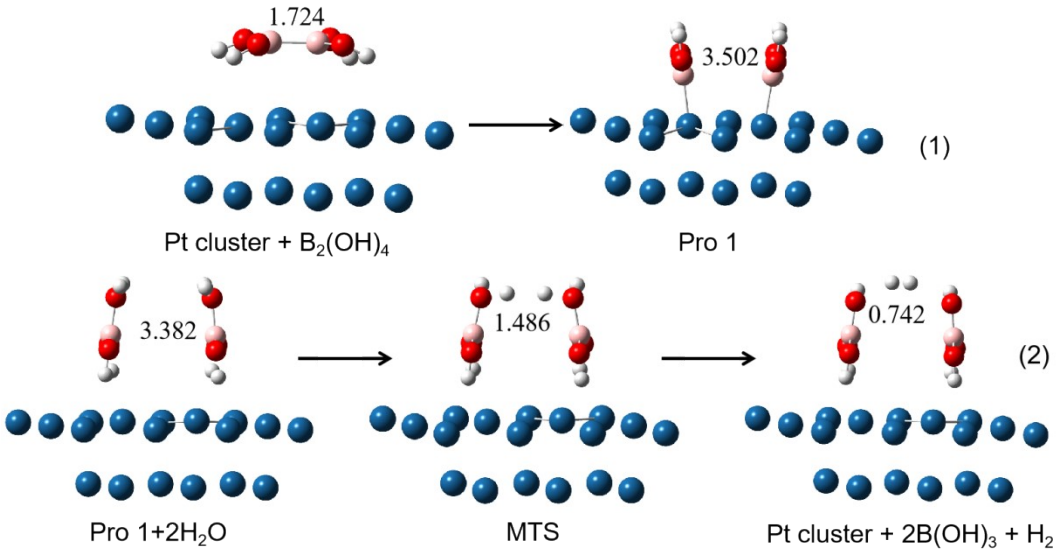
Scheme S2. Schematic diagram illustrating the formation of hydrogen and $B(OH)_3$ from tetrahydroxy diboron with water in the presenceof base, chemical structural formulas are replaced by optimized geometries. The typical distances in water are given in Å.

Table S2 Single point energy (SPE/hartree), ΔE and ΔG (kcal/mol) for formation of hydrogen from tetrahydroxy diboron with water at the presence of base.

Step 1	1+OH-	7		ΔE	ΔG
	-429.3446027	-429.3659159			-13.4
Step 2	7	8			
	-429.3659159	-429.3875538			-13.6
Step 3	8	BTS1	6+9		
	-429.3875538	-429.3467665	-429.3577965	25.6	18.7
Step 4	9+H2O	BTS2	5+OH-		
	-253.216026	-253.2140715	-253.2450886	1.2	-18.2
Step 5	5+H2O	BTS3	6+H2		
	-253.7663068	-253.7155015	-253.8012791	31.9	-21.9



Scheme S3 B-B bond disscociation reactions at the neutral, acid and base conditions



Scheme S4 Schematic diagram illustrating the formation of hydrogen from tetrahydroxy diboron with water in the presence of Pt nanoparticles

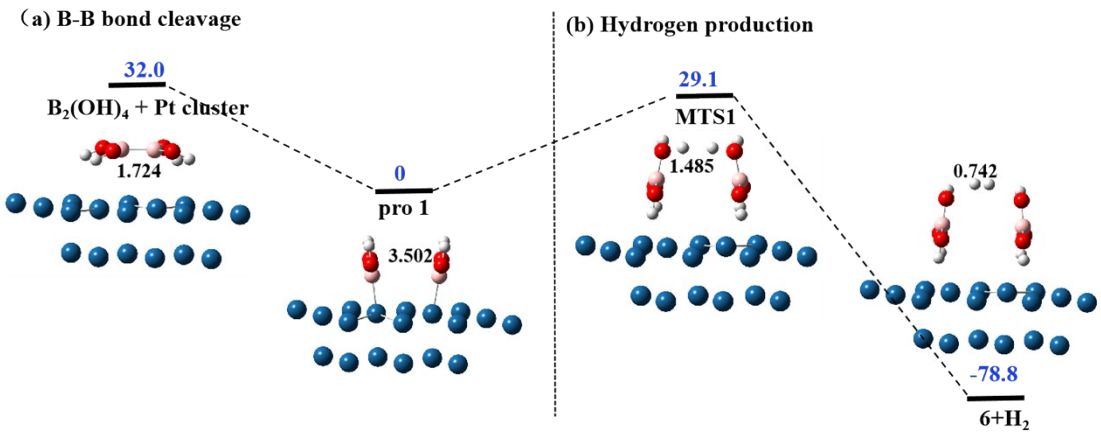


Figure S1 Relative electronic energy (blue) diagram for formation of hydrogen from $B_2(OH)_4$ with water in the presence of Pt nanoparticle

Table S3. Enthalpies of metal cluster adsorb on 1 and Pro1 and BDE with Pt, Au, Ag cluster

crystallographic plane	Enthalpy of Pt cluster adsorb on 1 (hartree)	Enthalpy of Pro1 (hartree)	BDE(kcal/mol)
111	-2502.818519	-2502.863411	-28.22
110	-2502.818143	-2502.863752	-28.6
100	-2502.648361	-2502.696346	-30.1
	Enthalpy of Au cluster adsorb on 1 (hartree)	Enthalpy of Pro1 (hartree)	BDE(kcal/mol)
111	-2798.172251	-2798.144612	17.3
110	-2798.172252	-2798.144564	17.4
100	-2798.017675	-2797.986305	19.7
	Enthalpy of Ag cluster adsorb on 1 (hartree)	Enthalpy of Pro1 (hartree)	BDE(kcal/mol)
111	-3000.260569	-3000.205002	34.9
110	-3000.273589	-3000.215539	36.4
100	-3000.125099	-3000.074628	31.7

Table S4 Electronic energies of Pt cluster, Pt cluster adsorb 1 and adsorption energy (E_{ads})

	Pt cluster (hartree)	Pt cluster adsorb 1 (hartree)	E_{ads} (kcal/mol)
111	-2149.500013	-2502.903137	-32.0
110	-2149.500013	-2502.903264	-32.0
100	-2149.223073	-2502.732051	-98.4
	Au cluster	Au cluster adsorb 1	E_{ads} (kcal/mol)
111	-2444.908082	-2798.258822	0.9
110	-2444.908082	-2798.258827	0.9
100	-2444.745954	-2798.103701	-3.5
	Ag cluster	Ag cluster adsorb 1	E_{ads} (kcal/mol)
111	-2646.995615	-3000.345682	1.3
110	-2647.005992	-3000.360075	-1.2
100	-2502.732051	-3000.212156	-4.0

Note: Electronic energies of $B_2(OH)_4$ is -353.3521916 hartree

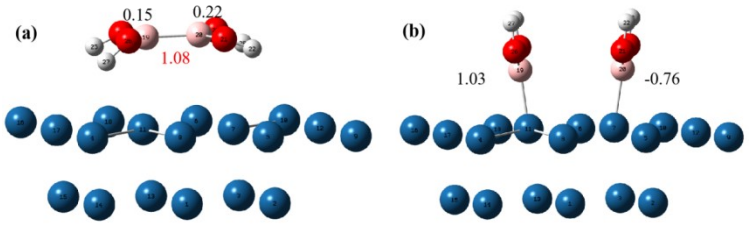


Figure S2 ADCH of B1 and B2 (black), B-B Mayer bond order (red) of before (a), after (b) B-B bond cleavage