Electronic Supplementary Information (ESI)

Theoretical Study of Al(III)-Catalyzed Conversion of Glyoxal to Glycolic Acid: Dual Activated 1,2-Hydride Shift Mechanism by Protonated $Al(OH)_3$ Species

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General Procedure for $Al(OH)_3$-catalyzed Conversion of Glyoxal (2) to Glycolic acid (1)

Into a glass-made cylindrical vessel were charged a 15.0% aqueous solution of glyoxal (500 g, 1292 mmol) and dried Aluminium hydroxide gel (243.7 mg, composition: Al_2O_3 54 wt%, 2.585 mmol aluminum metal, commercially available from Tomita Pharmaceutical Co., Ltd.). The glass vessel was inserted in a 1 L autoclave. The stirring blades of the autoclave were made of Teflon and its temperature measurement tube was also protected with glass. The autoclave was flushed with nitrogen and heated for 3 h at 165 ˚C with stirring. After completion of the reaction, the reaction mixture was cooled and discharged from the autoclave. Analysis by high-speed liquid chromatography revealed that the product mixture contained 1183 mmol of glycolic acid **1** (92%) along with 0.5 mmol of unreacted glyoxal **2** (<0.1%).

Computational Methods

Geometry optimizations and energies of all reactants, intermediates, transition states, and products were calculated with the Gaussian 03 programs[S-1] using density functional theory (DFT) methods at the B3LYP/6-31G(d,p) level followed by frequency calculations to determine the nature of the stationary points. All the transition states structures and the reaction coordinates (Hessian eigenvectors with negative eigenvalues) were examined visually. The intrinsic reaction coordinate (IRC) method was used to track minimum energy paths from transition structures to the corresponding local minima. Then, single point energy calculation at the B3LYP/6-311+G(d,p) level. Energies shown in the manuscript include zero-point energy corrections (not scaled) at the same level of the geometry optimizations. The energies computed for structures in water include the electronic energy at the B3LYP/6-311+G(d,p) // B3LYP/6-31G(d,p) level of theory plus the solvation energy calculated with the CPCM

solvation model as implemented in Gaussian 03 at the same level of theory with the UFF cavity model.

Additional Results

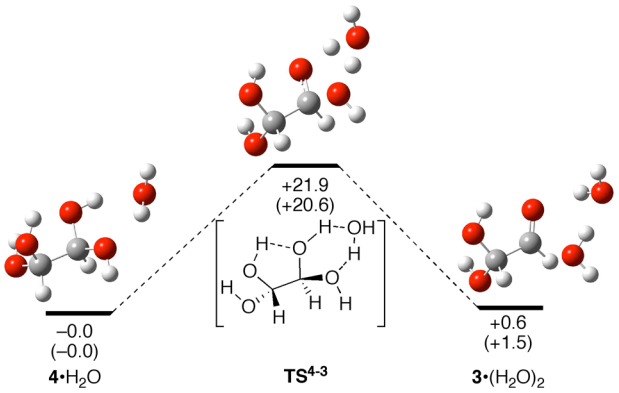

Fig. S-1 Possible reaction pathway of dihydrate **4** to monohydrate **3**. Values in parentheses include solvation energies in water using the CPCM/UFF model.

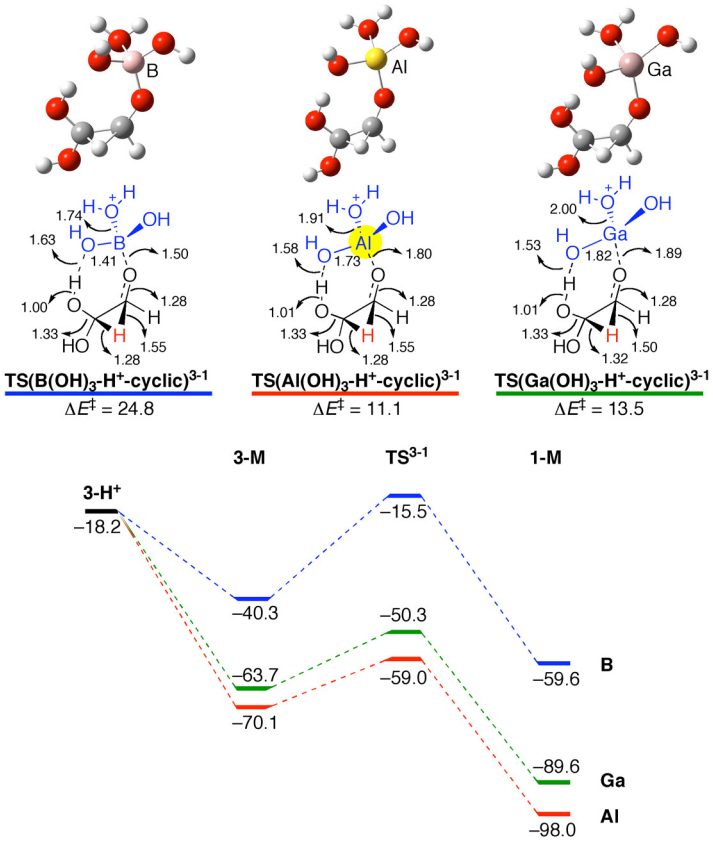

Fig. S-2 Transition states, possible reaction pathway, and energy profile of group 13 metal(III) catalysis.

Total Electron Energies and Cartesian Coordinates

TS$^{4-5}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -380.594504 A.U.

Zero-point correction = 0.086909 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -380.728301 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.564975	0.094879	-0.649988
2	6	0	0.617928	-0.231031	0.154212
3	8	0	-1.125715	1.283387	-0.509354
4	8	0	-1.553547	-1.200669	0.492203
5	1	0	-0.853070	-0.459677	-1.534734
6	8	0	1.620793	-0.975717	-0.462805
7	1	0	-0.404692	-0.995502	0.813020
8	8	0	1.090669	1.001680	0.722739
9	1	0	-2.189715	-0.751277	1.073644
10	1	0	-0.554920	1.743090	0.148625
11	1	0	2.081798	-0.407873	-1.103059
12	1	0	1.345285	0.818711	1.634896

TS$^{4-5}$ (water)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -380.613587 A.U.

Zero-point correction = 0.086162 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -380.754377 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.507693	0.251735	-0.720405

2	6	0	0.598313	-0.211787	0.105868
3	8	0	-1.076232	1.393364	-0.456954
4	8	0	-1.585955	-1.327339	0.445546
5	1	0	-0.845134	-0.259059	-1.612322
6	8	0	1.586173	-0.969664	-0.525228
7	1	0	-0.308469	-0.970726	0.652820
8	8	0	1.083513	0.887637	0.862295
9	1	0	-2.134003	-0.884833	1.114015
10	1	0	-0.554561	1.790636	0.280589
11	1	0	2.077744	-0.399928	-1.139204
12	1	0	1.160715	0.612243	1.786045

TS$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -304.201299 A.U.

Zero-point correction = 0.060306 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -304.302575 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.469789	0.026301	0.162080
2	6	0	0.733440	-0.788569	-0.013821
3	1	0	-0.173765	-0.411314	1.314938
4	1	0	0.821235	-1.867538	0.064033
5	8	0	-0.220714	1.281881	0.004580
6	8	0	1.770138	-0.035472	-0.100709
7	8	0	-1.690520	-0.528267	-0.155655
8	1	0	-2.320985	0.204277	-0.094032
9	1	0	1.220377	0.903053	-0.160221

TS$^{3-1}$ (water)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -304.221310 A.U.

Zero-point correction = 0.061737 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -304.326795 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-.458688	-.026934	.026159
2	6	0	.812103	-.708330	.027519
3	1	0	.186279	-.612501	1.230263
4	1	0	.775541	-1.800877	-.089082
5	8	0	-.398565	1.293643	.019450
6	8	0	1.866712	.000530	-.090744
7	8	0	-1.632501	-.619917	-.123776
8	1	0	-2.347889	-.026741	.163242
9	1	0	.580409	1.457656	-.065925

TS(H^+)$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -304.555234 A.U.

Zero-point correction = 0.074790 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -304.646906 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.484392	-0.022778	0.080060
2	6	0	0.781026	-0.671803	0.018200
3	1	0	0.034698	-0.408908	1.236734
4	1	0	0.818843	-1.758439	0.044581
5	8	0	-0.443286	1.313067	-0.004512
6	8	0	1.917843	-0.045219	-0.062576
7	8	0	-1.571696	-0.747935	-0.177714
8	1	0	-2.356492	-0.475288	0.327620
9	1	0	-1.314412	1.741157	0.004711

10	1	0	1.814667	0.909656	-0.244786

TS(H^+)$^{3-1}$ (water)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -304.660816 A.U.

Zero-point correction = 0.075449 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -304.754563 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.480081	-0.023282	0.072845
2	6	0	0.774757	-0.679096	0.016424
3	1	0	0.015594	-0.393395	1.218869
4	1	0	0.813011	-1.763017	0.041276
5	8	0	-0.437083	1.308910	-0.059139
6	8	0	1.914658	-0.049171	-0.049906
7	8	0	-1.579501	-0.745019	-0.168693
8	1	0	-2.348895	-0.409425	0.321677
9	1	0	-1.218586	1.754559	0.307539
10	1	0	1.786228	0.907790	-0.203060

TS($Al(OH)_2$)$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -697.917319 A.U.

Zero-point correction = 0.080926 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -698.088189 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.535938	-0.082003	0.196485
2	6	0	1.195471	1.027853	-0.652866

3	1	0	1.618031	1.118138	0.782493
4	1	0	1.965782	1.650386	-1.108687
5	13	0	-1.068481	-0.092056	0.027136
6	8	0	0.539856	-0.791990	0.655511
7	8	0	-0.054093	1.257016	-0.831775
8	8	0	-1.986218	0.734745	1.224415
9	1	0	-2.550905	0.238747	1.822952
10	8	0	-1.752542	-1.242290	-1.050908
11	1	0	-2.615239	-1.078490	-1.441198
12	8	0	2.787473	-0.596747	0.186405
13	1	0	2.808310	-1.293017	0.860769

TS(Al(OH)$_2$)$^{3-1}$ (water)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -697.941493 A.U.

Zero-point correction = 0.080683 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -698.115080 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.547883	-0.197332	-0.087986
2	6	0	-1.215964	1.194549	-0.172692
3	1	0	-1.650922	0.325513	-1.290648
4	1	0	-1.983868	1.964224	-0.219723
5	13	0	1.055363	-0.078325	0.027786
6	8	0	-0.528547	-1.033046	-0.011087
7	8	0	0.042989	1.486579	-0.217093
8	8	0	2.111558	-0.443660	-1.291177
9	1	0	1.739936	-0.917586	-2.043704
10	8	0	1.794006	0.042298	1.585042
11	1	0	2.526626	-0.556138	1.769768
12	8	0	-2.779436	-0.584532	0.298714
13	1	0	-2.892965	-1.522200	0.071960

TS(Al(OH)$_3$-cyclic)$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -774.357909 A.U.

Zero-point correction = 0.104400 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -774.561525 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.070850	-0.037212	0.079252
2	6	0	-1.206104	-1.160756	-0.200435
3	8	0	0.063112	-1.172314	-0.212679
4	8	0	-1.717613	1.203319	0.278662
5	8	0	-3.379168	-0.243035	-0.249929
6	13	0	1.499751	-0.015083	0.015064
7	8	0	2.115682	-0.549613	1.536262
8	8	0	2.443936	0.033618	-1.430022
9	8	0	0.667801	1.589155	0.059693
10	1	0	-1.841038	-0.828354	1.116512
11	1	0	-1.745749	-2.095045	-0.382141
12	1	0	2.753885	0.010060	1.987685
13	1	0	3.045346	-0.688988	-1.628685
14	1	0	-3.866971	0.523836	0.086423
15	1	0	-0.638733	1.414486	0.177389
16	1	0	0.908227	2.158850	-0.681820

TS(Al(OH)$_3$-cyclic)$^{3-1}$ (water)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -774.379472 A.U.

Zero-point correction = 0.104374 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -774.586700 A.U.

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	2.111281	-0.008935	-0.104143
2	6	0	1.226253	-1.148042	-0.063570
3	1	0	1.910162	-0.580468	-1.264424
4	8	0	-0.048548	-1.129549	-0.108257
5	8	0	1.738342	1.253033	-0.079355
6	8	0	3.429404	-0.139552	0.193815
7	13	0	-1.496841	0.011602	0.026688
8	8	0	-2.485345	-0.236392	-1.384531
9	8	0	-2.128882	-0.373844	1.603441
10	8	0	-0.730994	1.618356	-0.123318
11	1	0	1.724667	-2.121152	-0.062700
12	1	0	-2.840383	-1.125165	-1.501855
13	1	0	-2.953227	0.064207	1.845383
14	1	0	3.663007	-1.060460	0.387035
15	1	0	0.702994	1.404022	-0.104776
16	1	0	-0.965302	2.273641	0.546311

TS($Al(OH)_3$-open)$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -774.318209 A.U.

Zero-point correction = 0.105127 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -774.527664 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.388611	-0.060726	0.018514
2	6	0	0.995998	0.267630	-0.015681
3	13	0	-1.725119	0.009723	-0.010668
4	8	0	2.791508	-1.318166	0.005735
5	8	0	0.072927	-0.606376	-0.169756
6	8	0	-1.349715	1.675891	-0.456883
7	8	0	-2.686691	-0.967051	-1.072383

8	8	0	3.374342	0.847637	-0.057682
9	8	0	-2.159721	-0.131806	1.665604
10	1	0	1.593688	0.243243	1.193318
11	1	0	0.740717	1.337273	-0.086643
12	1	0	-1.937204	2.330613	-0.067067
13	1	0	-2.645265	-0.784670	-2.015016
14	1	0	3.023772	1.723709	-0.283047
15	1	0	3.746895	-1.357181	0.174610
16	1	0	-2.744903	-0.861842	1.888447

TS(Al-1)$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -849.347694 A.U.

Zero-point correction = 0.100523 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -849.549957 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.452041	-0.108376	-0.335472
2	6	0	2.271669	-0.459626	1.045979
3	1	0	2.489158	-1.412946	-0.087266
4	1	0	3.108156	-0.730153	1.689282
5	13	0	-0.099505	0.135653	0.131230
6	8	0	1.359749	0.235079	-0.980337
7	8	0	1.058544	-0.455650	1.477197
8	8	0	-1.356696	-1.019395	-0.306739
9	8	0	-1.120601	1.497556	0.401767
10	8	0	3.661122	0.247259	-0.811025
11	1	0	3.575449	0.363783	-1.770419
12	6	0	-2.561541	-0.405356	-0.251221
13	6	0	-2.463005	1.082357	0.166934
14	1	0	-3.074815	1.215808	1.068637
15	1	0	-2.922041	1.683480	-0.628649
16	8	0	-3.611786	-0.947030	-0.497725

TS(Al-1)$^{3-1}$ (water)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -849.378775 A.U.

Zero-point correction = 0.100529 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -849.584851 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.459475	-0.074883	-0.340825
2	6	0	2.275960	-0.545086	0.997923
3	1	0	2.512033	-1.372694	-0.207387
4	1	0	3.107539	-0.857995	1.624651
5	13	0	-0.073182	0.110241	0.138331
6	8	0	1.349465	0.295508	-0.971774
7	8	0	1.049280	-0.607364	1.418500
8	8	0	-1.385586	-0.980736	-0.394298
9	8	0	-1.114159	1.444723	0.528467
10	8	0	3.657278	0.356050	-0.766634
11	1	0	3.653104	0.390115	-1.737791
12	6	0	-2.566781	-0.364001	-0.277720
13	6	0	-2.460499	1.071777	0.267231
14	1	0	-3.068886	1.126798	1.179688
15	1	0	-2.918718	1.742545	-0.471325
16	8	0	-3.629107	-0.881774	-0.572484

TS(Al-1-OH)$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -925.790706 A.U.

Zero-point correction = 0.124410 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -926.027245 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.012650	-0.223958	-0.057203
2	6	0	1.972623	-1.222592	-0.002760
3	1	0	2.728534	-0.792957	-1.222374
4	1	0	2.345157	-2.249921	0.034678
5	13	0	-0.552398	0.303380	-0.039085
6	8	0	2.853530	1.079343	-0.068737
7	8	0	0.716825	-1.024866	-0.032051
8	8	0	-1.921936	-0.175915	-1.055235
9	8	0	-1.437486	0.438822	1.444959
10	8	0	4.241735	-0.661100	0.305495
11	1	0	4.871830	0.044683	0.092922
12	6	0	-3.030752	-0.290688	-0.295632
13	6	0	-2.782722	0.059075	1.192361
14	1	0	-3.064878	-0.817516	1.791088
15	1	0	-3.475995	0.867403	1.461940
16	8	0	-4.113695	-0.627824	-0.714383
17	1	0	1.874002	1.387239	-0.302515
18	8	0	0.498880	1.617622	-0.591198
19	1	0	0.168902	2.517437	-0.679039

TS(Al-1-OH)$^{3-1}$ (water)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -925.825078 A.U.

Zero-point correction = 0.124367 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -926.065279 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.001228	-0.234417	-0.039511
2	6	0	1.965715	-1.229479	-0.035704
3	1	0	2.756813	-0.754064	-1.207885

4	1	0	2.326451	-2.259052	-0.025763
5	13	0	-0.514879	0.323463	-0.065856
6	8	0	2.829679	1.079174	-0.021450
7	8	0	0.703083	-1.023311	-0.100652
8	8	0	-1.935875	-0.209755	-1.034644
9	8	0	-1.405353	0.446778	1.432927
10	8	0	4.214902	-0.668806	0.362212
11	1	0	4.886884	-0.043795	0.043500
12	6	0	-3.015696	-0.303061	-0.259326
13	6	0	-2.753551	0.069500	1.211478
14	1	0	-3.031564	-0.798000	1.826026
15	1	0	-3.443011	0.883861	1.473432
16	8	0	-4.113399	-0.649906	-0.664480
17	1	0	1.890681	1.378671	-0.315665
18	8	0	0.452262	1.651820	-0.678372
19	1	0	0.158609	2.564141	-0.563473

TS($Al(OH)_2$-H^+)$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -698.269165 A.U.

Zero-point correction = 0.093629 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -698.431856 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.626783	-0.091478	-0.219144
2	6	0	-1.322445	1.034654	0.618572
3	1	0	-1.781473	1.069758	-0.805840
4	1	0	-2.092456	1.637290	1.097926
5	13	0	0.946904	0.083703	-0.154772
6	8	0	-0.562179	-0.730262	-0.706106
7	8	0	-0.063971	1.321168	0.747329
8	8	0	2.341462	0.447134	-1.010063
9	1	0	2.532914	1.112189	-1.674529

10	8	0	1.782975	-1.108853	1.054297
11	1	0	1.409983	-1.882797	1.502711
12	8	0	-2.812783	-0.701075	-0.154644
13	1	0	-2.914022	-1.307736	-0.906940
14	1	0	2.746637	-1.200788	0.955646

TS($Al(OH)_2$-H^+)$^{3-1}$ (water)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -698.369566 A.U.

Zero-point correction = 0.092390 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -698.534317 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.733773	-1.156958	-0.669082
2	6	0	1.600850	0.058718	-0.219006
3	6	0	1.287468	-0.964311	0.729814
4	1	0	2.053666	-1.515398	1.269002
5	13	0	-0.970707	-0.060597	-0.122839
6	8	0	0.549560	0.658255	-0.779481
7	8	0	0.024396	-1.227589	0.893000
8	8	0	-2.289406	-0.611569	-1.040447
9	1	0	-2.230571	-1.436010	-1.535995
10	8	0	-1.734044	1.250154	0.947642
11	1	0	-2.696892	1.342063	1.042078
12	8	0	2.801471	0.653306	-0.228621
13	1	0	2.924221	1.110717	-1.077355
14	1	0	-1.310727	2.096447	1.166665

TS($Al(OH)_3$-cyclic-H^+)$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -774.722368 A.U.

Zero-point correction = 0.118588 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -774.919863 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.193612	-0.066598	-0.082113
2	6	0	1.267888	-1.173425	-0.022919
3	8	0	-0.006642	-1.099556	-0.050177
4	8	0	1.875676	1.220997	-0.026608
5	8	0	3.449594	-0.367674	0.298732
6	13	0	-1.411940	0.020578	-0.196306
7	8	0	-2.827118	-0.599171	-0.874086
8	8	0	-2.110580	0.087003	1.580928
9	8	0	-0.641449	1.544046	-0.496059
10	1	0	1.997901	-0.570812	-1.246566
11	1	0	1.733416	-2.161614	-0.041310
12	1	0	-2.975454	-1.024318	-1.721122
13	1	0	-3.010984	-0.273206	1.655449
14	1	0	4.034332	0.372944	0.069902
15	1	0	0.919741	1.429177	-0.274709
16	1	0	-1.042185	2.303093	-0.932788
17	1	0	-1.986384	0.812193	2.211479

TS($Al(OH)_3$-cyclic-H^+)$^{3-1}$ (water)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -774.818796 A.U.

Zero-point correction = 0.116759 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -775.017874 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.169115	-0.061158	-0.099634
2	6	0	1.246374	-1.160657	-0.034640

3	8	0	-0.028968	-1.104049	-0.127616
4	8	0	1.865090	1.229524	-0.134302
5	8	0	3.427847	-0.355338	0.305709
6	13	0	-1.411345	0.058651	-0.140086
7	8	0	-2.639347	-0.333489	-1.262729
8	8	0	-2.233515	-0.285219	1.510181
9	8	0	-0.647137	1.613796	0.045561
10	1	0	1.996634	-0.638965	-1.231649
11	1	0	1.717640	-2.142398	0.024931
12	1	0	-2.404781	-0.492223	-2.183932
13	1	0	-3.046964	-0.810841	1.579727
14	1	0	4.030083	0.320046	-0.046909
15	1	0	0.863497	1.428802	-0.107193
16	1	0	-1.032704	2.414127	-0.330937
17	1	0	-2.220614	0.368082	2.228288

TS(Al(OH)$_3$-open-H$^+$)$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -774.705612 A.U.

Zero-point correction = 0.117875 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -774.904517 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.471913	-0.066360	0.063971
2	6	0	1.130212	0.415680	-0.073564
3	13	0	-1.618868	0.141996	-0.192015
4	8	0	2.688011	-1.374456	0.010931
5	8	0	0.134774	-0.379837	-0.207312
6	8	0	-1.467214	1.800180	0.186988
7	8	0	-2.644986	-0.709298	-1.238546
8	8	0	3.569914	0.699509	-0.056786
9	8	0	-2.296088	-0.755094	1.370727
10	1	0	1.847473	0.259143	1.193622

11	1	0	0.977335	1.500757	-0.047436
12	1	0	-2.121286	2.477240	-0.005136
13	1	0	-2.618301	-0.770683	-2.195457
14	1	0	3.381534	1.604010	-0.351482
15	1	0	3.633822	-1.559970	0.136285
16	1	0	-2.960132	-1.425158	1.133361
17	1	0	-2.583192	-0.275235	2.161976

TS(Al-1-H^{+})$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -849.713643 A.U.

Zero-point correction = 0.113390 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -849.905227 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.505053	-0.196293	-0.315946
2	6	0	2.308883	-0.335968	1.100521
3	1	0	2.479994	-1.437781	0.089141
4	1	0	3.122495	-0.556003	1.789766
5	13	0	0.015534	0.265543	0.115922
6	8	0	1.400301	0.094782	-1.006899
7	8	0	1.085515	-0.222734	1.516462
8	8	0	-1.368353	-0.988197	-0.139173
9	8	0	-1.132846	1.551382	0.150565
10	8	0	3.710053	0.066824	-0.825148
11	1	0	3.680001	-0.001976	-1.793749
12	6	0	-2.472107	-0.373298	-0.160124
13	6	0	-2.459482	1.131979	0.004654
14	1	0	-3.077907	1.388495	0.877478
15	1	0	-2.945066	1.579860	-0.874799
16	8	0	-3.603078	-0.981520	-0.315806
17	1	0	-3.488284	-1.947482	-0.409455

TS(Al-1-H$^+$)$^{3-1}$ (water)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -849.805847 A.U.

Zero-point correction = 0.113512 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -850.000799 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.499551	-0.218372	-0.294620
2	6	0	2.316163	-0.195398	1.122949
3	1	0	2.488147	-1.391399	0.264816
4	1	0	3.138597	-0.318909	1.822686
5	13	0	0.008247	0.247333	0.097165
6	8	0	1.389996	-0.026601	-1.014224
7	8	0	1.091030	-0.050362	1.539250
8	8	0	-1.372929	-1.001593	-0.025011
9	8	0	-1.116813	1.564161	-0.011370
10	8	0	3.702510	-0.013245	-0.844869
11	1	0	3.690817	-0.323062	-1.766188
12	6	0	-2.471525	-0.384157	-0.120174
13	6	0	-2.450284	1.127485	-0.112791
14	1	0	-3.063462	1.470398	0.731373
15	1	0	-2.931403	1.478815	-1.034845
16	8	0	-3.605709	-0.990606	-0.223372
17	1	0	-3.498019	-1.962543	-0.216393

TS(Al-1-OH-H$^+$)$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -926.167279 A.U.

Zero-point correction = 0.138259 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -926.393117 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.061986	-0.299771	-0.082525
2	6	0	1.971832	-1.214512	0.164587
3	1	0	2.729770	-0.917679	-1.154685
4	1	0	2.267531	-2.260058	0.275517
5	13	0	-0.440892	0.432808	0.039092
6	8	0	2.961749	1.018057	-0.208908
7	8	0	0.725755	-0.932404	0.154946
8	8	0	-1.875785	-0.297616	-0.971824
9	8	0	-1.512452	0.658226	1.384695
10	8	0	4.269043	-0.750995	0.307690
11	1	0	4.953172	-0.151941	-0.032724
12	6	0	-2.905811	-0.332035	-0.247577
13	6	0	-2.810004	0.190862	1.170756
14	1	0	-3.084584	-0.627214	1.854048
15	1	0	-3.567604	0.978223	1.299098
16	8	0	-4.039763	-0.797642	-0.671517
17	1	0	2.046699	1.342373	-0.478057
18	8	0	0.499170	1.661195	-0.726323
19	1	0	0.234069	2.577955	-0.856710
20	1	0	-3.977211	-1.105988	-1.596214

TS(Al-1-OH-H^{+})$^{3-1}$ (water)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -926.256083 A.U.

Zero-point correction = 0.137390 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -926.484981 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.051323	-0.273061	-0.061526
2	6	0	1.991212	-1.216445	0.154583

3	1	0	2.712297	-0.907589	-1.131231
4	1	0	2.313940	-2.251911	0.263845
5	13	0	-0.434257	0.385996	0.020720
6	8	0	2.920125	1.043107	-0.189473
7	8	0	0.733179	-0.968399	0.153402
8	8	0	-1.873466	-0.330243	-0.960224
9	8	0	-1.478734	0.642903	1.395786
10	8	0	4.277079	-0.696803	0.310578
11	1	0	4.943415	-0.156052	-0.144894
12	6	0	-2.906463	-0.317221	-0.238648
13	6	0	-2.798666	0.224609	1.168899
14	1	0	-3.110661	-0.570862	1.859575
15	1	0	-3.520476	1.046427	1.270310
16	8	0	-4.053591	-0.749404	-0.651312
17	1	0	1.988846	1.339847	-0.467434
18	8	0	0.486615	1.622085	-0.771494
19	1	0	0.205907	2.545315	-0.786462
20	1	0	-4.002006	-1.076378	-1.571021

TS($B(OH)_3$-cyclic-H^+)$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -557.074276 A.U.

Zero-point correction = 0.125119 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -557.249012 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.797124	-0.034039	-0.139575
2	6	0	0.864592	-1.137126	-0.083821
3	8	0	-0.415122	-1.133960	-0.199218
4	8	0	1.506916	1.265325	-0.157345
5	8	0	3.019442	-0.337707	0.332845
6	5	0	-1.436201	-0.038603	-0.174668
7	8	0	-2.698335	-0.484230	-0.458732

8	8	0	-1.406885	0.355830	1.517733
9	8	0	-1.001438	1.178182	-0.740528
10	1	0	1.658682	-0.570079	-1.288842
11	1	0	1.342502	-2.117120	-0.049072
12	1	0	-2.793331	-1.431190	-0.611072
13	1	0	-2.158399	-0.058409	1.975462
14	1	0	3.638018	0.373260	0.097290
15	1	0	0.589094	1.434449	-0.505504
16	1	0	-1.617194	1.523942	-1.400251
17	1	0	-1.485275	1.317631	1.637662

TS($Ga(OH)_3$-cyclic-H^+)$^{3-1}$ (gas phase)

B3LYP/6-31G(d,p)

SCF Done: E(RB+HF-LYP) = -2455.14059 A.U.

Zero-point correction = 0.117035 A.U.

B3LYP/6-311+G(d,p)

SCF Done: E(RB+HF-LYP) = -2457.23139 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.363904	-0.065317	-0.031568
2	6	0	1.530773	-1.237198	-0.059759
3	8	0	0.250512	-1.280460	-0.126223
4	8	0	1.939992	1.192362	0.000832
5	8	0	3.616530	-0.267738	0.399283
6	31	0	-1.160923	-0.021933	-0.186693
7	8	0	-2.816154	-0.671121	-0.189748
8	8	0	-1.353528	0.544605	1.724521
9	8	0	-0.352243	1.360344	-1.047325
10	1	0	2.225985	-0.604233	-1.224443
11	1	0	2.073011	-2.185538	-0.055421
12	1	0	-3.047143	-1.322966	-0.863915
13	1	0	-2.213041	0.271931	2.090133
14	1	0	4.155641	0.513669	0.193012
15	1	0	1.085459	1.368483	-0.516688

16	1	0	-0.862014	2.044788	-1.498702
17	1	0	-1.078200	1.384958	2.120748

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