Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Theoretical investigation of dehydration of aquated $Al(OH)_2^+$ species in aqueous solution

*Zhaosheng Qian, Hui Feng, Wenjing Yang, Zhenjiang Zhang, Yingjie Wang and Shuping Bi**

School of Chemistry and Chemical Engineering, State Key Laboratory of Coordination Chemistry of China & Key Laboratory of MOE for Life Science, Nanjing University, Nanjing 210093, China

1. Structures for the gas-phase species of dehydration processes of $Al(H_2O)_4(OH)_2^+$ and $Al(H_2O)_3(OH)_2^+$

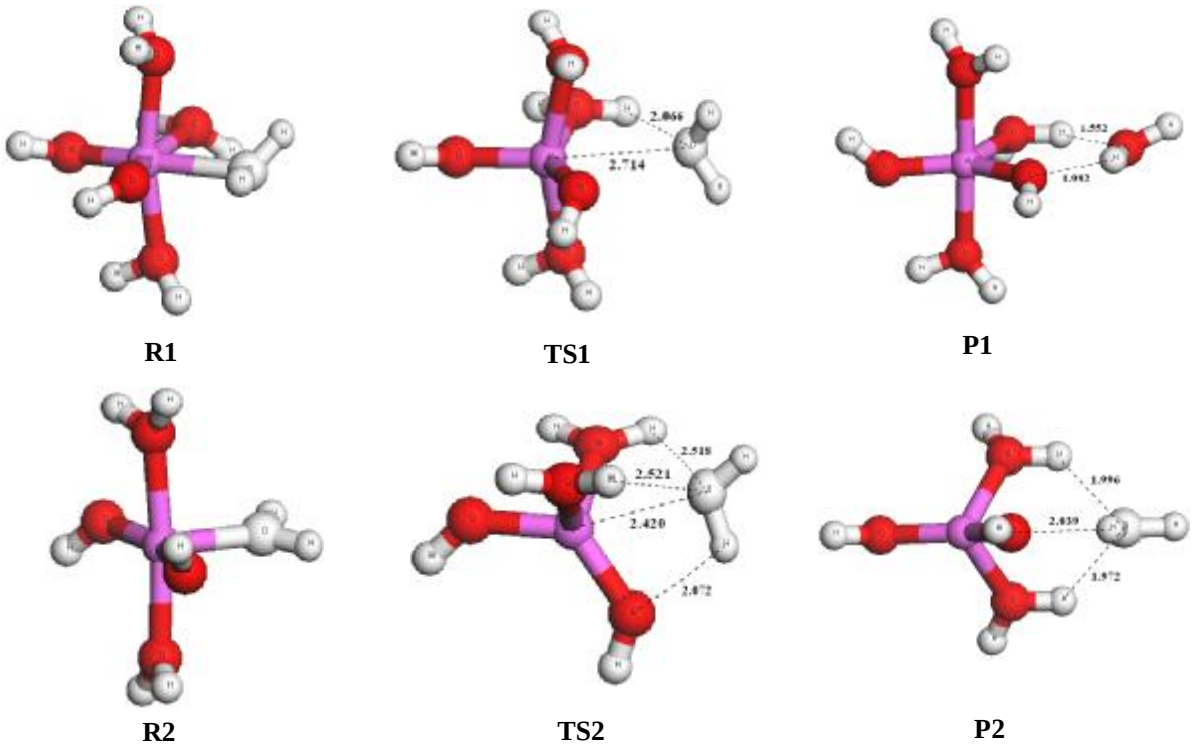

Figure S1. Structures of dehydration reactions of *cis*-$Al(H_2O)_4(OH)_2^+$ and $Al(H_2O)_3(OH)_2^+$ for gas-phase reaction system

2. Selected Structural Parameters (Å) for dehydration processes of *cis*-$Al(H_2O)_4(OH)_2^+$ and $Al(H_2O)_3(OH)_2^+$ in gas phase

Table S1. Selected Structural Parameters (Å) for dehydration processes of $Al(H_2O)_4(OH)_2^+$ and $Al(H_2O)_3(OH)_2^+$ in gas phase

complex	r(Al-O_I)	r(Al-O_L)	r(H-O_L)	r(Al-O)	∑r(Al-O)
R1	1.767,1.767,2.032,2.034,2.033,2.032	-	-	1.944	11.665
TS1	1.737,1.740,2.032,1.954,1.997	2.714	2.066	1.892	12.174
P1	1.726,1.723,2.044,1.991,1.932	3.401	1.992,1.552	1.883	12.817
R2	1.724,1.723,2.006,2.006,1.935	-	-	1.879	9.394
TS2	1.714,1.715,1.902,1.902	2.420	2.521,2.518	1.808	9.653
P2	1.718,1.690,1.917,1.847	3.039	1.996,1.972	1.797	10.265

3. IRC analysis for Reaction 1 and 2

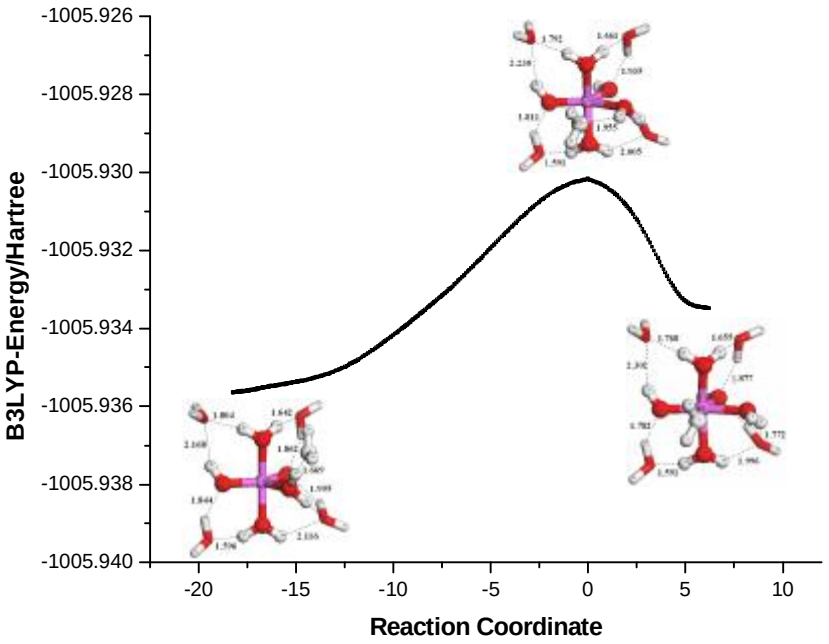

Figure S2. IRC analysis for Reaction 1

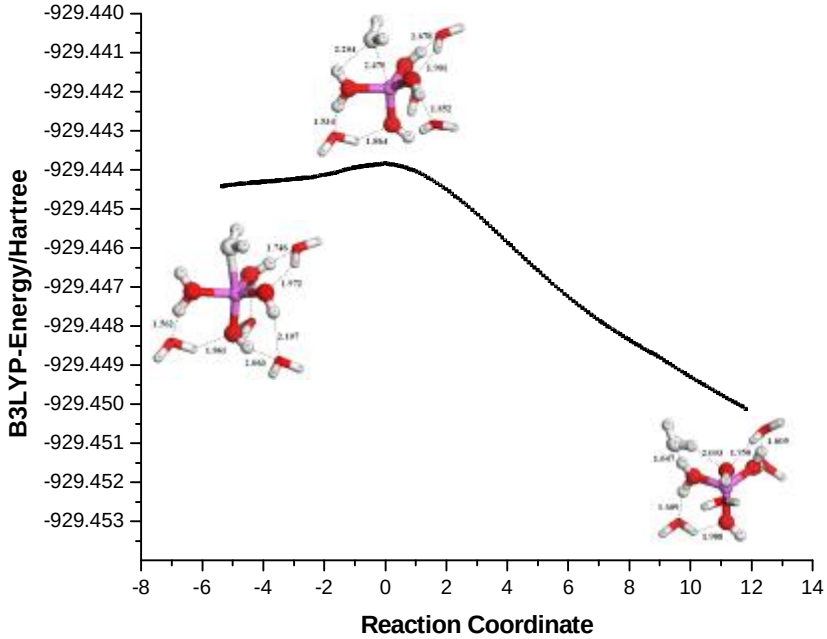

Figure S3. IRC analysis for Reaction 2

4. Cartersian coordinates of the supermolecular species at B3LYP/6-311+G** level

R_s1

O	-1.99970000	0.58400000	0.32340000
O	1.75000000	-0.38190000	0.69570000
O	0.29680000	1.73580000	-0.38500000
O	-0.22180000	-0.96040000	-1.26900000
O	-0.60720000	-1.57350000	1.21930000
O	-0.12490000	0.78440000	2.23630000
Al	-0.09220000	0.09780000	0.22700000
H	1.98630000	-1.28320000	0.33420000
H	-0.15040000	-0.46600000	-2.09150000
H	-0.76490000	-1.50590000	2.16820000
H	-1.35430000	-2.05810000	0.79680000
H	-0.73870000	1.51690000	2.37880000
H	0.72920000	1.04310000	2.60520000
H	1.19910000	1.99540000	-0.58860000
H	-2.60050000	-0.13540000	0.05750000
H	-2.22590000	1.41190000	-0.20700000
H	2.43150000	0.23600000	0.35040000
H	-1.07080000	2.67870000	-1.03110000
O	-2.04930000	2.68350000	-1.14740000
H	-2.37820000	3.58300000	-1.05970000

H	-1.79840000	-1.82950000	-1.16700000
O	-2.52530000	-2.04050000	-0.53310000
H	-3.12410000	-2.68480000	-0.92440000
H	1.16360000	-2.22550000	-1.21810000
O	2.02860000	-2.46440000	-0.82380000
H	2.10580000	-3.42270000	-0.79230000
H	4.07770000	2.02360000	-0.01910000
O	3.43530000	1.46370000	-0.47140000
H	3.85200000	1.20550000	-1.30300000

TS_s1

O	1.93070000	-0.62540000	0.12860000
O	-1.72190000	0.39770000	0.57670000
O	-0.35290000	-1.67050000	-0.54970000
O	0.25280000	1.17240000	-1.35770000
O	0.58840000	1.33110000	1.29080000
O	0.23900000	-0.91130000	2.63850000
Al	0.07210000	-0.03470000	-0.02550000
H	-1.98380000	1.32240000	0.30850000
H	0.20320000	0.83580000	-2.25730000
H	0.68250000	0.93540000	2.17410000
H	1.40090000	1.82300000	1.03990000
H	0.90640000	-1.59730000	2.75800000
H	-0.50760000	-1.16010000	3.19560000
H	-1.27050000	-1.94750000	-0.62290000
H	2.59440000	0.06060000	-0.06070000
H	2.14850000	-1.47410000	-0.37000000
H	-2.43500000	-0.21550000	0.29850000
H	0.97950000	-2.72860000	-1.17060000
O	1.95580000	-2.76450000	-1.28000000
H	2.25550000	-3.66960000	-1.15340000
H	1.89840000	2.01680000	-1.01070000
O	2.59280000	2.04920000	-0.31670000
H	3.23890000	2.72610000	-0.54380000
H	-1.15350000	2.48210000	-1.13320000
O	-2.00760000	2.65020000	-0.68940000
H	-2.09650000	3.59530000	-0.53320000
H	-4.02770000	-2.07070000	0.16220000
O	-3.45490000	-1.52010000	-0.38510000
H	-3.94760000	-1.35380000	-1.19820000

P_s1

O	1.97510400	-1.05186700	-0.17491600
O	-1.31725700	1.05147100	0.03826100
O	1.35379400	1.43840000	-0.26269700

O	-0.01271900	-0.72973600	1.69359000
O	-0.47212700	-1.16152600	-1.11780200
O	-2.80628900	-1.00271200	-2.37343100
Al	0.37598900	0.02365800	0.10162700
H	-1.95419700	0.83925700	0.77472000
H	0.64879900	-0.64017200	2.38631500
H	-1.34488900	-1.03194000	-1.56881200
H	-0.32101500	-2.10781100	-0.91553700
H	-2.94978600	-1.27350600	-3.28690800
H	-3.54423700	-0.43331500	-2.13136800
H	0.97261400	2.32053400	-0.29980900
H	2.01637800	-1.99688300	0.02426200
H	2.87158700	-0.61184900	-0.29148500
H	-1.23576000	2.02475700	-0.03522700
H	3.18221100	1.24835100	-0.40175800
O	3.91319600	0.59562800	-0.35136500
H	4.54525000	0.79089100	-1.05001400
H	0.07064400	-2.66096000	1.20143700
O	0.33825800	-3.21547300	0.44242500
H	0.20709100	-4.14066300	0.67507100
H	-1.69917600	-0.30504600	2.35931700
O	-2.49041300	0.25240800	2.21137400
H	-3.26244400	-0.17814300	2.58937300
H	-0.87488300	4.26234200	-0.99509900
O	-0.67326400	3.72945900	-0.21644700
H	-0.68230100	4.33819700	0.53243000

R_s2

O	-1.27990000	0.64710000	0.28030000
O	1.21830000	0.91140000	-1.10080000
O	-1.01290000	-1.53650000	-1.14200000
O	1.53740000	-1.59830000	-1.26440000
O	0.84880000	-0.90070000	1.25210000
Al	0.13350000	-0.26560000	-0.36890000
H	0.89470000	1.81640000	-1.19610000
H	-2.02270000	-1.45580000	-1.00450000
H	-0.73400000	-2.33810000	-1.59700000
H	2.06680000	-1.01510000	-1.83060000
H	2.16310000	-2.07700000	-0.70410000
H	1.79330000	-0.62190000	1.35720000
H	0.30470000	-0.65360000	2.06540000
H	-1.22860000	1.59900000	0.10830000
H	-0.20540000	4.05120000	-0.14810000
O	-0.48970000	3.33450000	-0.72820000
H	-0.95700000	3.76580000	-1.45380000

O	-0.81850000	0.04520000	2.94110000
H	-1.35410000	0.39920000	2.20460000
H	-1.40470000	-0.31140000	3.61630000
O	3.22910000	0.04010000	0.61680000
H	4.03890000	0.41010000	0.98310000
H	2.85050000	0.67860000	-0.01950000
O	-3.33800000	-0.93670000	-0.43020000
H	-4.15730000	-0.73610000	-0.89420000
H	-2.94050000	-0.10550000	-0.09100000

TS_s2

O	-0.97290000	-0.98400000	-1.08200000
O	1.72270000	-0.31240000	0.04590000
O	-1.02360000	-0.95530000	1.53020000
O	0.80160000	0.66410000	2.34090000
O	-0.41870000	1.61400000	-0.02820000
Al	-0.01060000	-0.19360000	0.17140000
H	2.16690000	-1.00770000	-0.46920000
H	-1.84130000	-1.52100000	1.29640000
H	-0.91820000	-0.70930000	2.45660000
H	1.72090000	0.38790000	2.21930000
H	0.83140000	1.59820000	2.58030000
H	0.40000000	2.18090000	-0.08240000
H	-1.12520000	1.91170000	-0.66550000
H	-0.59430000	-1.20160000	-1.93610000
H	3.52230000	-2.16680000	-2.24900000
O	2.92350000	-2.33670000	-1.51360000
H	3.20260000	-3.18040000	-1.14100000
O	-2.29970000	2.31120000	-1.72520000
H	-2.78390000	1.61640000	-2.18540000
H	-2.87690000	3.08190000	-1.68610000
O	2.05690000	2.40680000	0.06160000
H	2.66790000	2.99440000	-0.39390000
H	2.34360000	1.47970000	-0.07830000
O	-2.90840000	-2.14740000	0.39050000
H	-3.20390000	-3.06370000	0.38760000
H	-2.42390000	-1.96470000	-0.44350000

P_s2

O	0.49130000	1.27910000	-1.62090000
O	-1.47730000	-0.60310000	-0.06190000
O	0.47920000	1.14550000	1.12430000
O	-1.57730000	0.56200000	2.57080000
O	1.17320000	-1.31010000	-0.31880000
Al	0.06160000	0.15600000	-0.37820000

H	-2.28810000	-0.36860000	-0.55050000
H	0.82620000	2.07390000	0.95300000
H	-0.18240000	1.08530000	1.86930000
H	-1.91350000	-0.07180000	1.91450000
H	-1.79230000	0.23820000	3.45130000
H	0.73670000	-2.17630000	-0.05100000
H	2.16700000	-1.34430000	-0.28620000
H	0.44150000	1.14150000	-2.56760000
H	-4.30930000	-0.47240000	-2.04340000
O	-3.79770000	0.08990000	-1.45190000
H	-4.36360000	0.84060000	-1.24210000
O	3.79390000	-1.40800000	-0.23630000
H	4.38350000	-1.57330000	-0.98010000
H	4.34590000	-1.28950000	0.54440000
O	-0.46080000	-3.11920000	0.45090000
H	-0.72290000	-4.00460000	0.17990000
H	-1.19850000	-2.50230000	0.27980000
O	1.44180000	3.26600000	0.06510000
H	1.33450000	4.22140000	0.10310000
H	1.20330000	2.95710000	-0.82790000