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Supplementary Materials

Catalytic Effect of a Single Water Molecule on the OH + CH_2NH Reaction

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Table S1. Optimized geometries of reactants, complexes, transition states and products obtained using BHandHLYP/aug-cc-pVTZ level.

CH_2NH

C	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.08477011
H	0.96762571	0.00000000	-0.48169887
N	-1.03324157	0.00000000	-0.70674090
H	-1.87115562	0.00000000	-0.14360145

OH

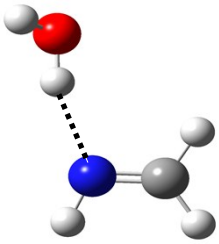
O	0.00000000	0.00000000	0.10694300
H	0.00000000	0.00000000	-0.85554200

H_2O

H	0.00000000	0.75771600	-0.45886800
O	0.00000000	0.00000000	0.11471700
H	0.00000000	-0.75771600	-0.45886800

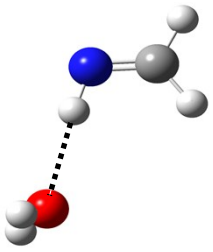
$CH_2NH\cdots H_2O$ (RC-1)

C	-1.44441400	-0.49052200	0.01977300
H	-2.52257800	-0.58072200	-0.03388200
H	-0.87661000	-1.40653900	0.08994900
N	-0.83206000	0.60212900	0.00297300
H	-1.45291400	1.39354500	-0.06787000
O	1.96449500	-0.15460000	-0.08154500
H	2.51872600	0.27875900	0.55547600
H	1.10831900	0.27998400	-0.03076100



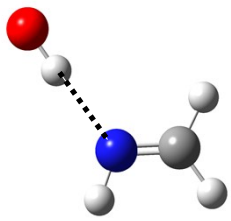
$CH_2NH\cdots H_2O$-1 (RC-2)

C	-1.71160200	0.39222500	-0.00001300
H	-1.28293200	1.38970700	-0.00002200
H	-2.79172700	0.33213000	-0.00002100
N	-1.03384500	-0.65973000	0.00000600
H	-0.04348800	-0.45691100	0.00001200
O	2.06148600	0.15401900	0.00000600
H	2.56639000	-0.11618000	-0.75897200
H	2.56640100	-0.11613900	0.75899100



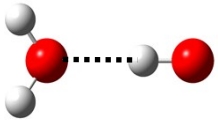
$CH_2NH\cdots OH$ (RC-3)

C	-1.55780000	-0.38001200	0.00000700
H	-2.61415000	-0.14202900	0.00009800
H	-1.29349000	-1.42707500	-0.00005600
N	-0.64817200	0.48062400	-0.00002700
H	-1.00830800	1.42277200	0.00003900
O	2.19418900	-0.12987200	0.00001100
H	1.24644300	0.10101200	-0.00002400



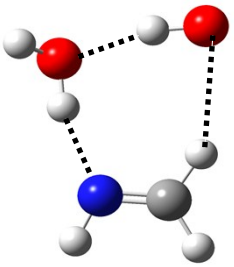
$H_2O\cdots HO$ (RC-4)

O	1.60976500	0.00000000	0.01043000
H	0.64116500	-0.00000300	-0.02712100
O	-1.24838900	-0.00000100	-0.05224600
H	-1.76609300	-0.76252000	0.18082800
H	-1.76608200	0.76252700	0.18082600



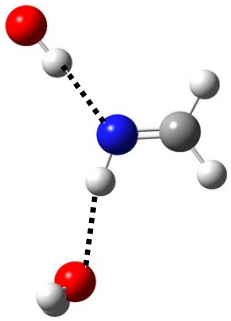
$CH_2NH\cdots H_2O\cdots OH$ (PRC-1)

C	-1.60784300	-0.81117000	-0.00863800
H	-2.51691700	-1.39897900	-0.03962700
H	-0.66880900	-1.34480500	-0.01015700
N	-1.59825200	0.44315500	0.02609300
H	-2.52503600	0.83980900	0.02020500
O	1.06349400	1.36155200	-0.09143900
H	1.29696600	2.06867100	0.49717600
H	0.10616400	1.22763100	-0.01986500
O	1.86398900	-1.27610700	0.02196600
H	1.72258800	-0.31095000	-0.02276900



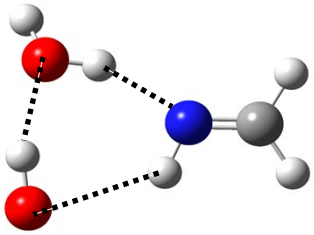
$CH_2NH\cdots H_2O\cdots OH$ (PRC-2)

C	0.22247900	1.68946800	0.00002000
H	-0.71483400	2.23346700	-0.00009800
H	1.12871000	2.27828700	0.00024000
N	0.29412500	0.44002400	-0.00008800
H	-0.61942000	0.00688000	-0.00028100
O	2.69826700	-1.13958400	0.00003500
H	1.87912200	-0.60453300	-0.00001600
O	-2.60172000	-0.70628100	-0.00000700
H	-2.91983900	-1.18172900	0.75962300
H	-2.91986200	-1.18242000	-0.75919400



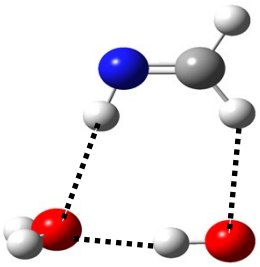
$CH_2NH\cdots H_2O\cdots OH$ (PRC-3)

H	-0.65784200	-0.90803600	-0.00804300
H	-2.98310800	0.77965800	0.01991300
O	1.34328300	1.32289900	-0.08686200
H	1.55618800	2.02750400	0.51245600
H	0.39607700	1.14874100	-0.00965000
O	1.77419600	-1.41712700	0.01590100
H	1.82933500	-0.44408100	-0.01783600
N	-1.13036400	-0.01465100	0.01702400
C	-2.37731500	-0.11452300	-0.00151600
H	-2.90404300	-1.06026900	-0.03922500

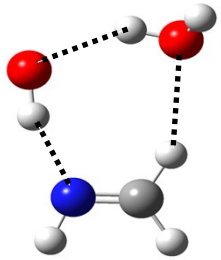


$CH_2NH\cdots H_2O\cdots OH$ (PRC-4)

C	1.99188100	0.34298100	-0.00003900
H	3.04290200	0.59769200	0.00030000
H	1.29300800	1.17324200	-0.00043100
N	1.65445100	-0.86331100	0.00004000
O	-1.70756800	-1.06366700	-0.00001100
H	-2.01079100	-1.54426600	0.76295000
H	-2.01129700	-1.54423600	-0.76279100
O	-1.17190900	1.74455000	0.00003600
H	-1.46013400	0.81936700	0.00002700
H	0.64968000	-0.96356800	-0.00030200

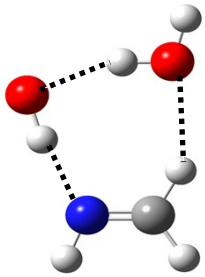


$CH_2NH\cdots H_2O\cdots OH$ (PRC-5)



C	-1.46309300	-0.94331300	-0.03047200
H	-2.23915800	-1.69797500	-0.06768800
H	-0.43665800	-1.27825000	-0.06338500
N	-1.70194600	0.28611000	0.04819000
H	-2.68815900	0.49330300	0.07196800
O	0.74260900	1.66279600	-0.02061400
H	-0.19394000	1.37648300	0.03515600
O	1.97166100	-0.92696600	-0.06331700
H	2.56482700	-1.15021300	0.64453200
H	1.97111000	0.02712400	-0.10363100

$CH_2NH\cdots H_2O\cdots OH$ (PRC-6)



C	1.50605300	-0.88871200	-0.00105300
H	2.37383800	-1.53664600	-0.00040800
H	0.53153800	-1.35331800	-0.00312600
N	1.58670600	0.36422800	0.00048100
H	2.53812700	0.69707200	0.00237000
O	-0.88410300	1.67096900	-0.00059000
H	0.03886300	1.32504800	0.00001100
O	-1.77028800	-1.04779900	0.00257800
H	-1.69169400	-0.09102900	0.00126700
H	-2.69879800	-1.24380600	-0.01306400

TS1

O	-0.48082400	1.37762500	-0.24385800
H	0.45531400	1.14309500	-0.16675100
C	-1.27665600	-0.26881600	0.46503200
H	-2.27899800	0.07591400	0.26946100
H	-0.91122600	-0.14450200	1.46893500
N	-0.63873900	-1.06918300	-0.32269500
H	-1.11867400	-1.17258000	-1.20390600
O	1.96776700	-0.09448200	0.17461200
H	2.76624900	-0.29695300	-0.29736000
H	1.32290500	-0.77294100	-0.04773400

TS2

C	1.46099800	0.18008100	-0.00105500
H	2.45409300	0.61822400	-0.04008400
H	0.55092100	1.05350200	0.02084500
N	1.14888300	-1.01354100	0.01724700
H	1.92540000	-1.66017000	-0.00763700
O	-1.73888100	-0.81737100	-0.09505300
H	-2.24961000	-1.21893300	0.59761200
H	-0.84765900	-1.17177400	-0.02378500
O	-0.45271000	1.73802000	0.01599200
H	-1.10858600	1.02825800	-0.02886700

TS3

O	0.33024500	1.39027300	-0.10868300
H	0.69640700	1.36896400	-0.99642200
C	1.16769600	-0.34209100	0.57153800
H	0.46334600	-0.39874200	1.38773900

H	2.13552300	0.07694600	0.78832100
N	0.99444600	-0.94942300	-0.54935200
H	0.05958500	-1.33320800	-0.59506100
O	-1.95845500	-0.32044400	0.07489000
H	-2.86631900	-0.04720000	0.11902100
H	-1.43016400	0.47310400	-0.01702000

TS4

C	-0.62100800	0.42761000	0.00000000
H	-0.31372300	1.47172600	-0.00000500
H	-1.82498900	0.31798100	0.00000000
N	0.08542800	-0.57745800	0.00000600
H	1.08350600	-0.39681000	0.00000500
O	-3.10302500	0.04658800	-0.00000200
H	-3.02455800	-0.90883100	-0.00000100
O	3.09566900	0.10079300	-0.00000300
H	3.63332800	-0.09330900	-0.75987400
H	3.63333200	-0.09326200	0.75987600

TS5

O	-2.89542000	-0.20808400	-0.03108700
H	-3.01807300	-0.80832500	0.70660000
C	-0.37797400	-0.18206400	-0.12496800
H	-1.58405300	-0.22702800	-0.13239400
H	0.12730400	-1.13017600	-0.25767500
N	0.22774600	0.88421300	0.01414700
H	-0.35822800	1.69711900	0.13527200
O	2.85689200	-0.40095700	0.08971800
H	3.62592500	-0.04119500	-0.33493800
H	2.18896300	0.28482600	0.06487100

TS6

H	0.35972600	0.46641200	0.36690800
H	2.61672200	-1.31637800	-0.24332700
O	-2.05393800	-0.65083300	-0.18288800
H	-2.77811600	-0.94415900	0.35743200
H	-1.27723700	-1.10833000	0.13365400
O	-0.22295000	1.59633000	0.03115400
H	-1.07659200	1.20060100	-0.18291800
N	0.87043800	-0.53042400	0.35865600
C	1.98551400	-0.43864800	-0.18627000
H	2.36445700	0.48273300	-0.61084400

TS7

O	2.51462000	-0.60866900	-0.05265100
H	2.55579300	-0.94883400	0.84342200
C	0.20441800	1.24208900	0.01161600
H	1.12498800	1.80748900	0.07269100
H	-0.73324700	1.78025100	0.05883700
N	0.17141900	0.00366100	-0.11354100
H	1.17083400	-0.44737000	-0.19467200
O	-2.71365400	-0.40562400	0.10966000
H	-3.17247500	-0.97896300	-0.49225700
H	-1.78006400	-0.57638900	-0.01900000

TS8

C	-1.60872700	-0.04727500	0.00000100
H	-2.64763200	0.26271100	0.00000500
H	-0.84215700	0.88384600	0.00000100
N	-1.25793900	-1.22973100	-0.00000100
O	1.92392800	-0.59744200	-0.00000100
H	2.46775600	-0.77079600	-0.76119300
H	2.46772800	-0.77075300	0.76122200
O	0.12760800	1.78381700	0.00000000
H	0.85516100	1.15416700	-0.00002600
H	-0.25520800	-1.35841500	-0.00000400

H_2O

H	0.00000000	0.75771600	-0.45886800
O	0.00000000	0.00000000	0.11471700
H	0.00000000	-0.75771600	-0.45886800

cis-CHNH

C	0.10973300	0.62950400	0.00000000
H	-0.66902500	1.38869200	0.00000000
N	0.10973300	-0.57998600	0.00000000
H	-0.75750600	-1.10581800	0.00000000

trans-CHNH

C	0.00062400	0.63869700	0.00000000
N	0.00062400	-0.57829000	0.00000000
H	-0.88250300	-1.06713500	0.00000000
H	0.87439400	1.28298000	0.00000000

$NHCH_2$-OH

C	-0.05045300	0.48608100	0.02855300
H	-0.12050100	1.06014000	0.96031000
N	-1.13623600	-0.41621100	-0.02766300
H	-1.99626400	0.11907700	-0.01179800
H	-0.09147100	1.20479800	-0.79030600
O	1.17517000	-0.16708600	-0.05251900
H	1.06324400	-1.05032800	0.28426600

Table S2: Electronic energies, Zero-point energies (ZPE), and zero-point corrected energies of two-body complexes, three body complexes and transition states computed using at CC/a-Z//B&H/a-Z.

Species	E_e(Hartree)	ZPE(Hartree)	E+ZPE(Hartree)
$CH_2NH\cdots H_2O$(RC-1)	-170.8323046	0.066701	-170.7656036
$CH_2NH\cdots H_2O$-1(RC-2)	-170.826836	0.065237	-170.761599
$CH_2NH\cdots OH$ (RC-3)	-170.1368859	0.053529	-170.0833569
$H_2O\cdots HO$ (RC-4)	-151.9969154	0.034091	-151.9628244
CH_2NH--H_2O--OH (PRC-1)	-246.4918688	0.079496	-246.4123728
$CH_2NH\cdots H_2O\cdots OH$ (PRC-2)	-246.4813978	0.077226	-246.4041718
$CH_2NH\cdots H_2O\cdots OH$ (PRC-3)	-246.4894763	0.079173	-246.4103033
$CH_2NH\cdots H_2O\cdots OH$ (PRC-4)	-246.4813978	0.077226	-246.4041718
$CH_2NH\cdots H_2O\cdots OH$ (TS1)	-246.48478	0.080270	-246.40451
$CH_2NH\cdots H_2O\cdots OH$ (TS2)	-246.4783359	0.073481	-246.4048549
$CH_2NH\cdots H_2O\cdots OH$ (TS3)	-246.481461	0.079249	-246.402212
$CH_2NH\cdots H_2O\cdots OH$ (TS4)	-246.4694045	0.070829	-246.3985755
$CH_2NH\cdots H_2O\cdots OH$ (TS5)	-246.4751072	0.072062	-246.4030452
CH_2NH--H_2O--OH (TS6)	-246.4802734	0.072635	-246.4076384
$CH_2NH\cdots H_2O\cdots OH$ (TS7)	-246.4778823	0.072261	-246.4056213
$CH_2NH\cdots H_2O\cdots OH$ (TS8)	-246.4768595	0.072689	-246.4041705

Table S3: BSSE corrected energies of two-body complexes, three body complexes were computed using at CC/a-Z//B&H/a-Z.

Species	**BSSE (Hartree)**	**BSSE (kcal/mol)**
$CH_2NH\cdots H_2O$ (RC-1)	0.002238479	1.40
$CH_2NH\cdots H_2O$-1 (RC-2)	0.002033429	1.27
$CH_2NH\cdots HO$ (RC-3)	0.002092781	1.30
$H_2O\cdots HO$ (RC-4)	0.002199618	1.38
$CH_2NH\cdots H_2O\cdots OH$ (PRC-1)	0.003542650	2.20
$CH_2NH\cdots H_2O\cdots OH$ (PRC-2)	0.004239076	2.66
$CH_2NH\cdots H_2O\cdots OH$ (PRC-3)	0.003287296	2.06
$CH_2NH\cdots H_2O\cdots OH$ (PRC-4)	0.002232818	1.40

Table S4. Vibrational frequencies of reactants, complexes, transition states and products obatined using BHandHLYP/aug-cc-pVTZ level.

Reactants and Products

CH_2NH	OH	H_2O	cis-CHNH	trans-CHNH	CH_2NH-OH
1107.6	3866.8	1674.7	887.0	932.1	153.0
1157.4		3961.3	951.1	1002.1	466.6
1203.9		4064.1	1067.9	1219.2	532.5
1415.3			1915.3	1873.4	928.3
1543.2			3079.5	3122.9	1006.4
1789.4			3463.1	3568.7	1145.6
3120.7					1212.4
3214.3					1280.8
3579.0					1385.7
					1479.5
					1517.4
					2989.5
					3068.9
					3554.1
					3969.1

Complexes

RC-1	RC-2	RC-3	RC-4	PRC-1	PRC-2	PRC-3	PRC-4	PRC-5	PRC-6
46.8	34.0	68.6	115.3	68.9	20.8	65.5	33.4	59.96	75.03
97.9	54.6	147.0	167.7	76.1	60.2	69.7	48.4	76.17	93.51
158.6	82.3	203.5	193.4	125.7	74.3	129.2	66.1	112.45	103.88
201.5	123.8	583.1	425.1	196.9	84.7	173.3	73.8	130.79	150.09
397.3	171.9	669.4	636.9	202.5	131.7	189.4	93.7	140.44	190.15
660.9	272.2	1122.3	1675.6	223.5	157.0	214.9	181.7	196.94	203.46
1116.2	1137.2	1169.3	3730.0	245.6	192.5	223.1	190.0	240.92	251.79
1171.1	1155.0	1193.3	3959.7	457.7	233.3	430.4	223.3	295.89	391.74
1193.6	1255.5	1429.9	4060.9	529.2	306.9	499.3	295.2	452.29	463.43
1425.7	1445.7	1545.2		710.2	616.2	667.3	436.3	652.53	625.12
1542.5	1542.0	1794.4		853.3	716.8	828.8	629.6	807.41	876.71
1705.4	1677.4	3143.3		1131.6	1152.5	1141.1	1131.6	1133.5	1141.69
1790.5	1789.3	3236.4		1181.6	1167.1	1167.5	1172.1	1181.46	1182.58
3138.5	3111.0	3593.4		1201.0	1252.3	1216.1	1231.2	1206.03	1205.14
3236.5	3200.2	3597.4		1437.7	1465.2	1431.1	1437.4	1438.29	1441.93
3597.1	3568.9			1551.6	1544.0	1546.1	1546.7	1554.68	1555.35
3765.4	3957.0			1709.0	1680.1	1696.0	1678.2	1704.16	1700.82
4034.2	4057.6			1785.3	1796.1	1800.1	1787.4	1785.24	1783.74
				3139.5	3133.3	3138.7	3115.2	3137.77	3140.64
				3243.8	3223.4	3229.1	3207.6	3244.1	3252.31
				3567.3	3535.6	3570.1	3582.7	3487.72	3395.45

				3599.0	3565.3	3607.6	3734.2	3600.05	3601.1
				3626.8	3956.2	3686.0	3952.2	3907.13	3805.56
				4031.0	4055.5	4033.0	4050.6	4035.4	4037.49

Transtion states

TS1	**TS2**	**TS3**	**TS4**	**TS5**	**TS6**	**TS7**	**TS8**
93.3	105.8	90.1	36.3	37.4	38.7	30.4	67.0
153.9	170.6	112.4	39.6	51.0	98.5	61.3	90.1
180.5	179.3	119.4	68.4	89.6	150.1	104.5	127.1
206.8	201.8	178.5	108.6	91.3	165.1	132.2	144.4
301.2	249.1	273.9	137.5	123.7	192.4	171.8	208.4
413.8	311.1	343.1	159.0	205.7	273.0	198.6	211.0
526.2	390.1	378.8	192.2	338.8	407.5	338.1	263.8
574.4	581.9	542.1	205.9	388.8	461.3	400.3	363.3
684.6	602.9	599.9	413.4	537.8	508.2	541.5	540.4
1008.0	666.7	807.4	661.4	671.0	699.5	759.6	686.2
1088.8	956.7	1103.7	842.0	861.7	896.6	831.2	891.1
1108.8	1027.1	1118.7	1102.0	1059.7	1141.9	1156.4	1103.7
1125.4	1091.9	1137.4	1110.4	1103.5	1178.3	1188.3	1132.8
1419.3	1113.3	1424.6	1119.2	1218.2	1214.8	1286.0	1138.8
1440.6	1312.8	1459.5	1306.6	1354.0	1398.1	1400.3	1340.9
1630.3	1564.8	1632.8	1532.4	1431.6	1503.5	1498.0	1534.6
1686.3	1694.4	1682.7	1678.7	1692.5	1682.6	1691.8	1678.2
3188.1	1824.2	3173.1	1845.7	1813.9	1791.8	1788.8	1827.2
3285.8	3127.2	3271.7	3098.2	3188.2	3131.3	3139.8	3158.9
3596.3	3556.8	3569.6	3511.6	3589.6	3214.7	3229.3	3566.9
3716.5	3719.9	3845.6	3907.7	3842.5	3797.2	3836.7	3832.0
3772.0	3776.9	3880.1	3957.0	3903.7	3899.9	3899.9	3950.9
4033.7	4029.1	4041.3	4056.9	4037.5	4038.0	4034.5	4049.0

Table S5-a: Rate coeffcients (k_2 in s^{-1})) computed using CVT/SCT method.

TS1	***TS2***	***TS3***	***TS4***	***TS5***	***TS6***	***TS7***	***TS8***
1.64E+06	1.40E+09	1.22E+06	3.75E+09	1.04E+11	3.99E+08	1.26E+06	1.67E+11
5.59E+06	1.54E+09	3.27E+06	4.18E+09	1.23E+11	9.22E+08	3.18E+06	1.64E+11
1.50E+07	1.71E+09	7.22E+06	4.65E+09	1.42E+11	2.06E+09	8.92E+06	1.63E+11
3.39E+07	1.91E+09	1.38E+07	5.16E+09	1.63E+11	3.61E+09	2.36E+07	1.62E+11
6.69E+07	2.15E+09	2.36E+07	5.72E+09	1.87E+11	6.84E+09	5.62E+07	1.63E+11
1.19E+08	2.43E+09	3.70E+07	6.34E+09	2.12E+11	1.20E+10	1.20E+08	1.63E+11
1.95E+08	2.75E+09	5.43E+07	7.03E+09	2.40E+11	1.96E+10	2.34E+08	1.65E+11
3.00E+08	3.12E+09	7.54E+07	7.79E+09	2.70E+11	3.03E+10	4.20E+08	1.66E+11
4.36E+08	3.55E+09	1.00E+08	8.65E+09	3.03E+11	4.46E+10	7.07E+08	1.69E+11

Table S5-b: Rate coeffcients (k_2 in s^{-1})) computed using TST/Eckart method.

TS1	***TS2***	***TS3***	***TS4***	***TS5***	***TS6***	***TS7***	***TS8***
4.38E+06	3.55E+09	2.60E+06	7.03E+07	2.10E+08	4.55E+11	1.20E+10	7.22E+10
1.49E+07	4.47E+09	6.50E+06	1.28E+08	8.26E+08	5.35E+11	3.01E+10	7.01E+10
4.00E+07	5.59E+09	1.35E+07	2.28E+08	2.51E+09	6.19E+11	6.39E+10	6.84E+10
9.00E+07	6.94E+09	2.44E+07	3.96E+08	6.34E+09	7.05E+11	1.20E+11	6.71E+10
1.77E+08	8.56E+09	3.98E+07	6.67E+08	1.39E+10	7.94E+11	2.06E+11	6.61E+10
3.15E+08	1.05E+10	6.02E+07	1.09E+09	2.71E+10	8.86E+11	3.27E+11	6.53E+10
5.17E+08	1.27E+10	8.57E+07	1.70E+09	4.85E+10	9.81E+11	4.90E+11	6.48E+10
7.94E+08	1.52E+10	1.16E+08	2.59E+09	8.08E+10	1.08E+12	7.00E+11	6.44E+10
1.16E+09	1.81E+10	1.52E+08	3.81E+09	1.27E+11	1.18E+12	9.61E+11	6.43E+10

Table 6a: BSSE corrected calculated equilibrium constants (cm^3 $molecule^{-1}$) for the formation of two-body complex.

Temp	$K_{eq(1)}$ (CH_2NH+ H_2O→ RC-1)	$K_{eq(4)}$ (H_2O+HO →RC-4)
200	2.33E-21	4.07E-21
225	9.05E-22	1.85E-21
250	4.33E-22	9.92E-22
275	2.40E-22	6.02E-22
300	1.44E-22	4.01E-22
325	1.01E-22	2.86E-22
350	7.34E-23	2.17E-22
375	5.61E-23	1.71E-22
400	4.48E-23	1.40E-22

Table 6b: BSSE corrected calculated equilibrium constants (cm^3 $molecule^{-1}$) for the formation of three-body complex.

T (K)	$K_{eq(a)}$ (OH + RC-1 →PRC-1)	$K_{eq(b)}$ (OH + RC-1 →PRC-2)	$K_{eq(c)}$ (OH + RC-2 →PRC-2)	$K_{eq(d)}$ (OH + RC-1 →PRC-3)	$K_{eq(e)}$ (OH + RC-1 →PRC-4)	$K_{eq(f)}$ (CH_2NH + RC-4 →PRC-1)	$K_{eq(g)}$ (CH_2NH + RC-4 →PRC-3	$K_{eq(h)}$ (CH_2NH+ RC-4 →PRC-4)
200	3.61E-20	8.03E-22	3.65E-20	4.31E-22	1.54E-23	1.96E-20	2.34E-22	8.83E-24
225	6.58E-21	3.82E-22	7.98E-21	1.36E-22	1.16E-23	3.08E-21	6.39E-23	5.7E-24
250	1.69E-21	2.14E-22	2.38E-21	5.47E-23	9.48E-24	7.09E-22	2.29E-23	4.13E-24
275	5.60E-22	1.36E-22	8.89E-22	2.61E-23	8.16E-24	2.16E-22	1.00E-23	3.26E-24
300	2.24E-22	9.38E-23	3.94E-22	1.42E-23	7.31E-24	8.07E-23	5.1E-24	2.73E-24
325	1.04E-22	6.95E-23	1.99E-22	8.49E-24	6.75E-24	3.55E-23	2.91E-24	2.38E-24
350	5.40E-23	5.43E-23	1.12E-22	5.52E-24	6.38E-24	1.78E-23	1.81E-24	2.13E-24
375	3.08E-23	4.42E-23	6.84E-23	3.83E-24	6.15E-24	9.81E-24	1.22E-24	2.01E-24
400	1.89E-23	3.72E-23	4.47E-23	2.79E-24	6.00E-24	5.88E-24	8.68E-25	1.91E-24

Table S6-c: BSSE corrected rate coeffcients (k_2 in s^{-1})) computed using CVT/SCT method.

TS1	TS2	TS3	TS4	TS5	TS6	TS7	TS8
6.97E+05	1.56E+09	8.74E+05	6.77E+09	1.78E+11	4.59E+08	1.66E+06	6.97E+11
2.37E+06	1.71E+09	1.88E+06	7.47E+09	2.07E+11	9.85E+08	3.69E+06	5.93E+11
6.93E+06	1.89E+09	3.87E+06	8.23E+09	2.39E+11	1.80E+09	9.62E+06	5.22E+11
1.74E+07	2.12E+09	7.42E+06	9.06E+09	2.74E+11	3.65E+09	1.48E+08	4.72E+11
3.80E+07	2.38E+09	1.32E+07	9.98E+09	3.11E+11	6.86E+09	3.36E+08	4.35E+11
7.44E+07	2.70E+09	2.20E+07	1.10E+10	3.52E+11	1.20E+10	6.93E+08	4.07E+11
1.33E+08	3.06E+09	3.46E+07	1.21E+10	3.96E+11	1.95E+10	1.31E+09	3.86E+11
2.21E+08	3.49E+09	5.17E+07	1.34E+10	4.44E+11	3.01E+10	2.31E+09	3.70E+11
3.45E+08	3.97E+09	7.40E+07	1.48E+10	4.96E+11	4.43E+10	3.81E+09	3.58E+11

Table S7a: Equilibrium constant (cm^3 $molecule^{-1}$), H_2O concertation (cm^{-3} molecule) and rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) of the $CH_2NH + OH \rightarrow$ Products, $CH_2NH\cdots H_2O + OH \rightarrow$ PRCs$\rightarrow$ Products and $CH_2NH + H_2O\cdots OH \rightarrow$ PRCs$\rightarrow$ Products computed using TST/Eckart method.

T (K)	$K_{eq(1)}$ ($CH_2NH + H_2O \rightarrow CH_2NH \cdots H_2O$	$K_{eq(4)}$ ($H_2O + OH \rightarrow OH \cdots H_2O$)	$[H_2O]$	k_a^{eff}	k_b^{eff}	k_{total}^{eff}
200	7.89E-20	1.38E-19	1.09E+14	1.82E-14	1.74E-14	3.56E-14
225	2.07E-20	4.23E-20	2.04E+15	2.27E-14	2.17E-14	4.45E-14
250	7.24E-21	1.66E-20	2.12E+16	3.05E-14	2.91E-14	5.96E-14
275	3.11E-21	7.80E-21	1.44E+17	4.23E-14	4.03E-14	8.27E-14
300	1.56E-21	4.19E-21	7.10E+17	5.99E-14	5.69E-14	1.17E-13
325	8.85E-22	2.50E-21	2.74E+18	8.60E-14	8.12E-14	1.67E-13
350	5.49E-22	1.62E-21	8.72E+18	1.23E-13	1.16E-13	2.40E-13
375	3.67E-22	1.12E-21	2.38E+19	1.77E-13	1.66E-13	3.44E-13
400	2.61E-22	8.19E-22	5.72E+19	2.53E-13	2.37E-13	4.91E-13

Table S7b: BSSE corrected equilibrium constant (cm^3 $molecule^{-1}$), and rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) of the $CH_2NH + OH \rightarrow$ Products, CH_2NH --$H_2O + OH \rightarrow$ PRCs$\rightarrow$ Products and $CH_2NH + H_2O$--$OH \rightarrow$ PRCs$\rightarrow$ Products computed using CVT/SCT method.

T(K)	$K_{eq(1)}$ ($CH_2NH + H_2O \rightarrow CH_2NH \cdots H_2O$	$K_{eq(4)}$ ($H_2O + OH \rightarrow OH \cdots H_2O$)	k_a^{eff}	k_b^{eff}	k_{total}^{eff}
200	2.329E-21	4.074E-21	9.96E-17	2.38E-17	1.23E-16
225	9.05E-22	1.849E-21	1.96E-16	5.14E-17	2.47E-16
250	4.325E-22	9.918E-22	3.75E-16	1.09E-16	4.85E-16
275	2.402E-22	6.018E-22	7.03E-16	2.27E-16	9.31E-16
300	1.494E-22	4.006E-22	1.29E-15	4.59E-16	1.75E-15
325	1.012E-22	2.865E-22	2.31E-15	8.89E-16	3.21E-15
350	7.339E-23	2.167E-22	4.03E-15	1.67E-15	5.72E-15
375	5.613E-23	1.715E-22	6.85E-15	3.00E-15	9.90E-15
400	4.483E-23	1.407E-22	1.13E-14	5.23E-15	1.66E-14

Error and Uncertainties

The computed thermochemistry using CC/a-Z//B&H/a-Z level is not greater than ~2 kcal/mol and is probably of the order of 1 kcal/mol, which results in a factor of ~5 uncertainty in the predicted total rate constants at 300 K. Previous studies on reaction systems analogous to the present work report similar accuracy.[7,8]

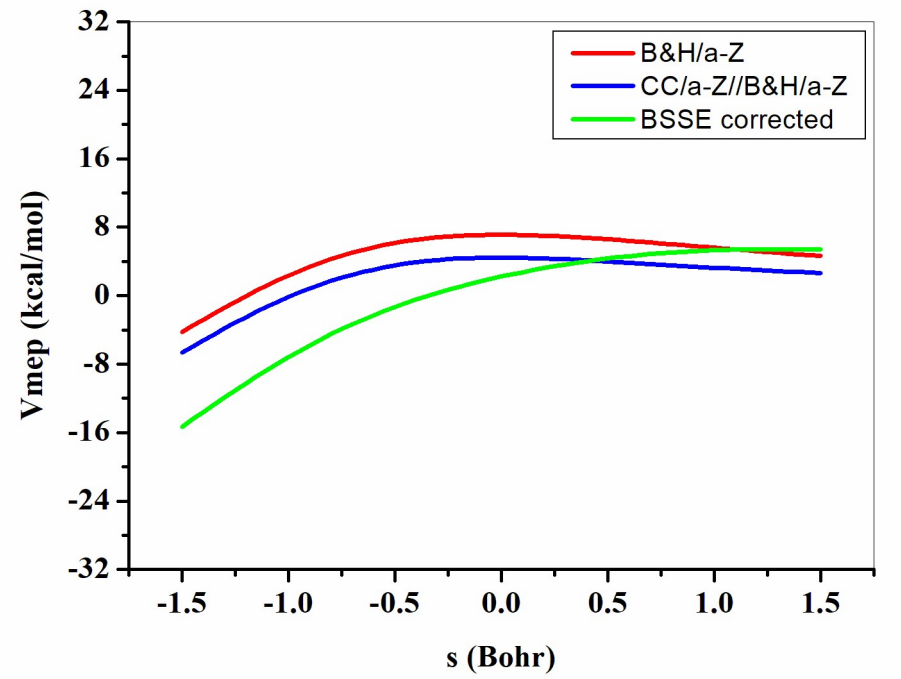


Figure S1-a: Minimum energy pathway (TS1) obtained from CVT/SCT and CVT/SCT/ISPE methodologies using B&H/a-Z, CC/a-Z//B&H/a-Z and CC/a-Z+ BSSE correction //B&H/a-Z.

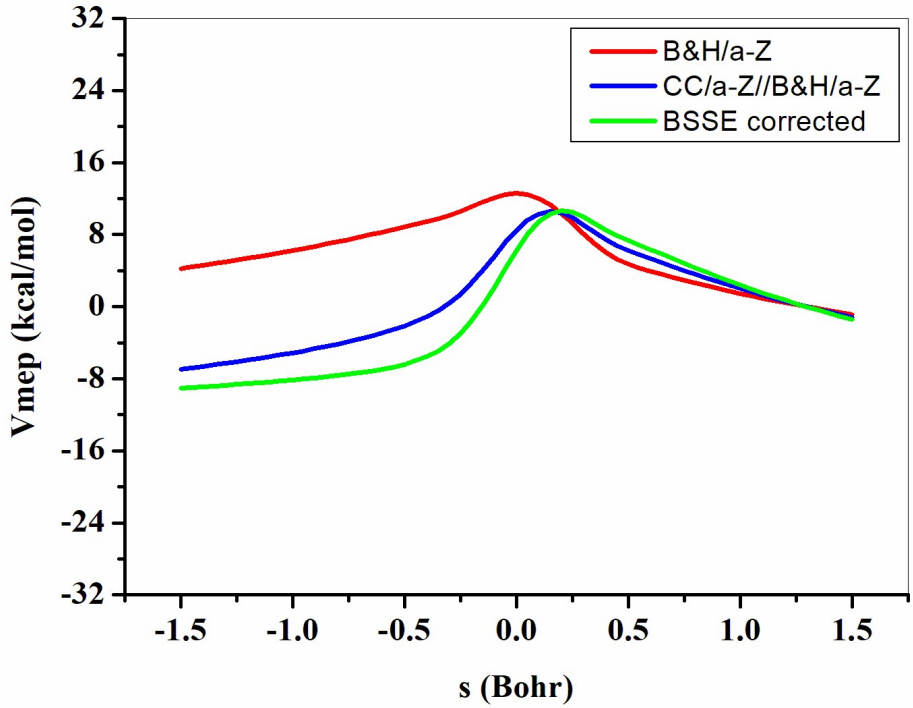


Figure S1-b: Minimum energy pathway (TS2) obtained from CVT/SCT and CVT/SCT/ISPE methodologies using B&H/a-Z, CC/a-Z//B&H/a-Z and CC/a-Z//B&H/a-Z + BSSE correction.

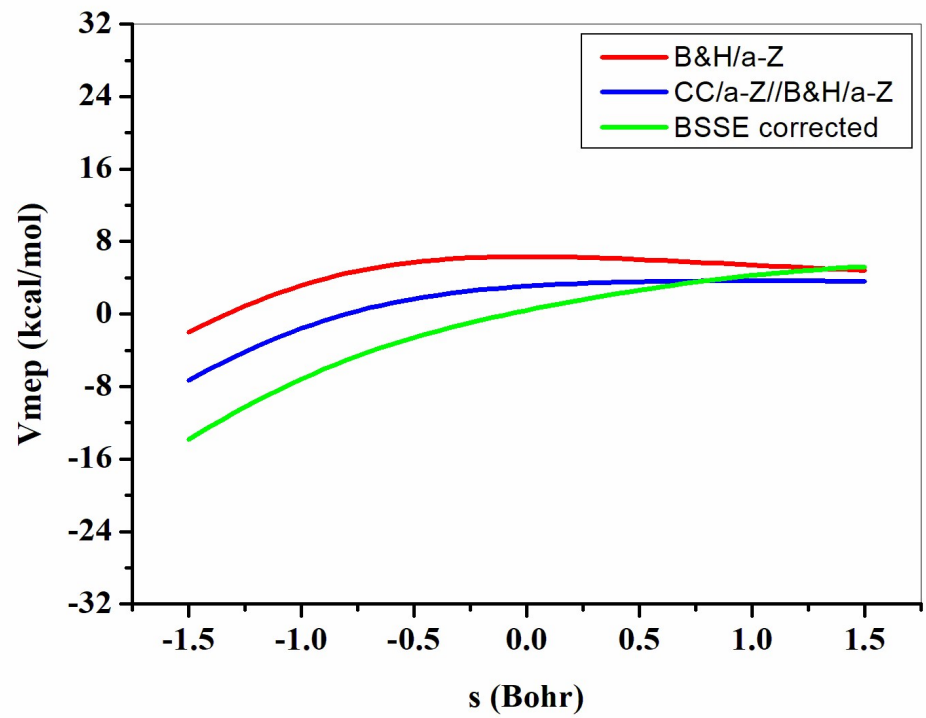


Figure S1-c: Minimum energy pathway (TS3) obtained from CVT/SCT and CVT/SCT/ISPE methodologies using B&H/a-Z, CC/a-Z//B&H/a-Z and CC/a-Z + BSSE correction //B&H/a-Z.

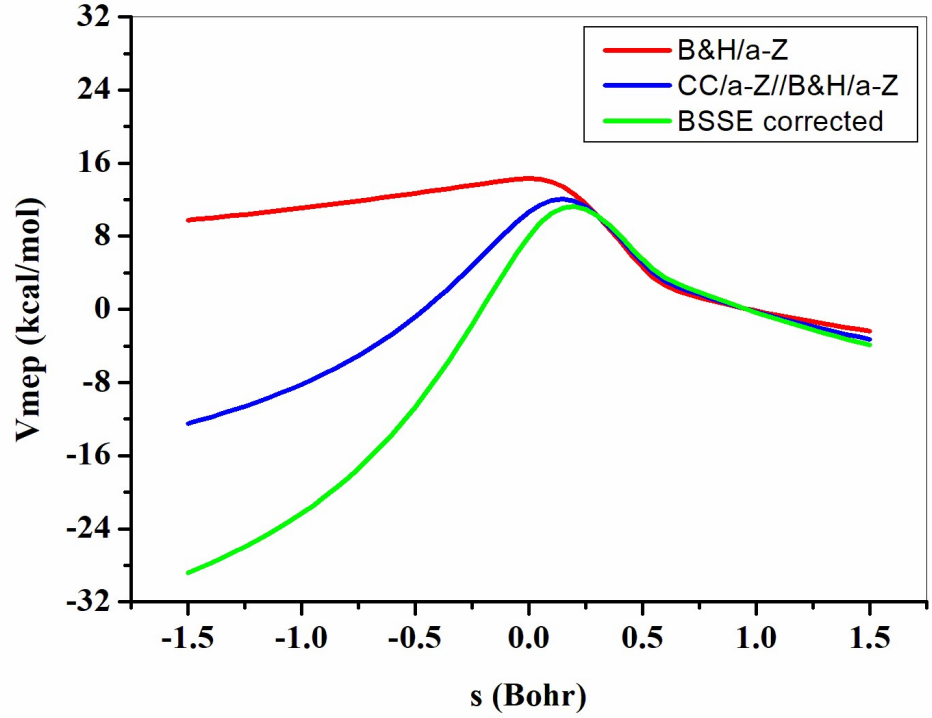


Figure S1-d: Minimum energy pathway (TS4) obtained from CVT/SCT and CVT/SCT/ISPE methodologies using B&H/a-Z, CC/a-Z//B&H/a-Z and CC/a-Z+ BSSE correction //B&H/a-Z.

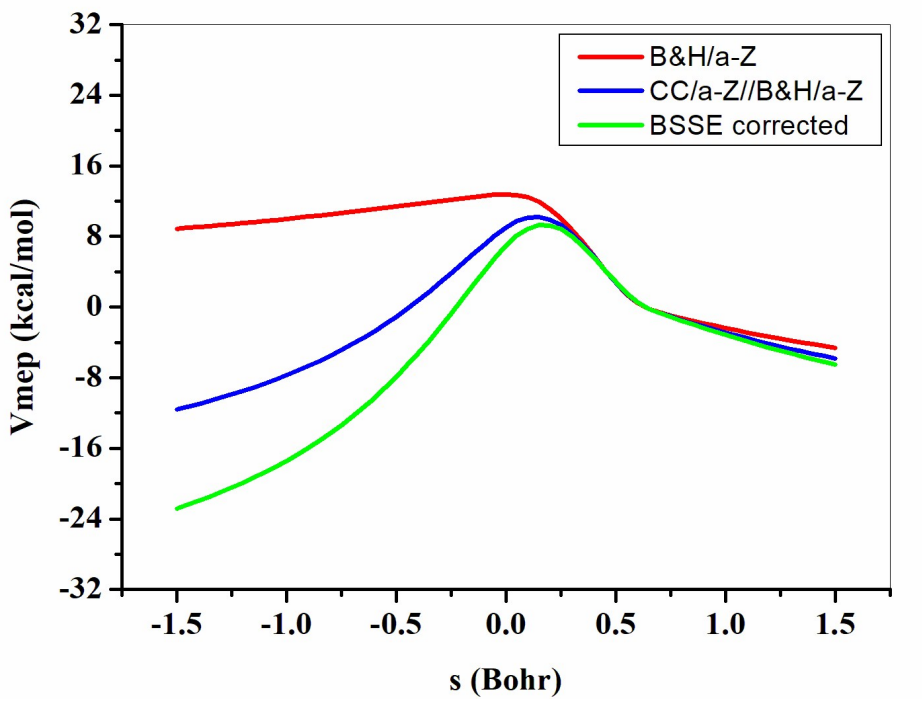


Figure S1-e: Minimum energy pathway (TS5) obtained from CVT/SCT and CVT/SCT/ISPE methodologies using B&H/a-Z, CC/a-Z//B&H/a-Z and CC/a-Z + BSSE correction //B&H/a-Z.

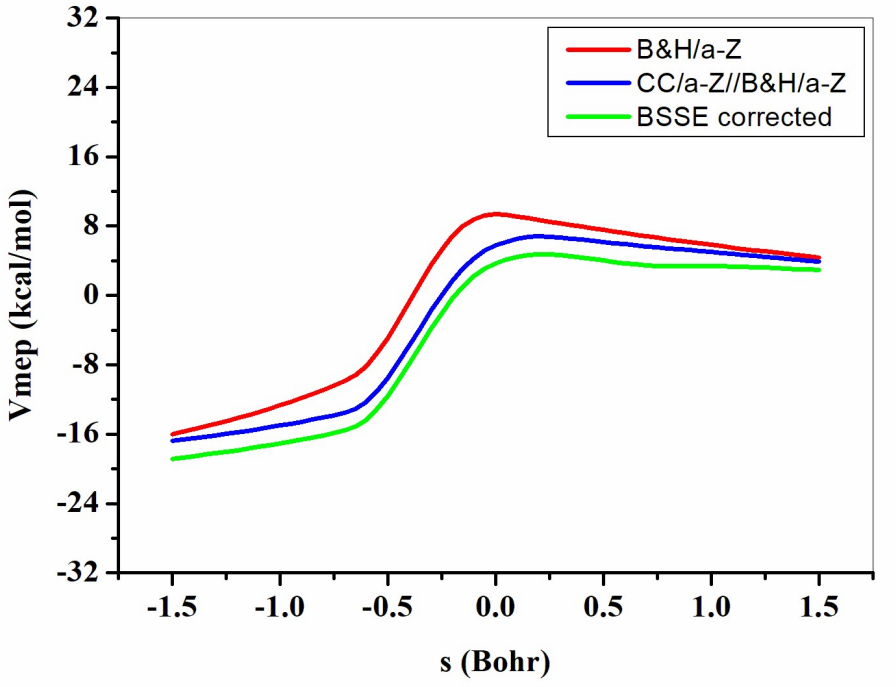


Figure S1-f: Minimum energy pathway (TS6) obtained from CVT/SCT and CVT/SCT/ISPE methodologies using B&H/a-Z, CC/a-Z//B&H/a-Z and CC/a-Z + BSSE correction //B&H/a-Z.

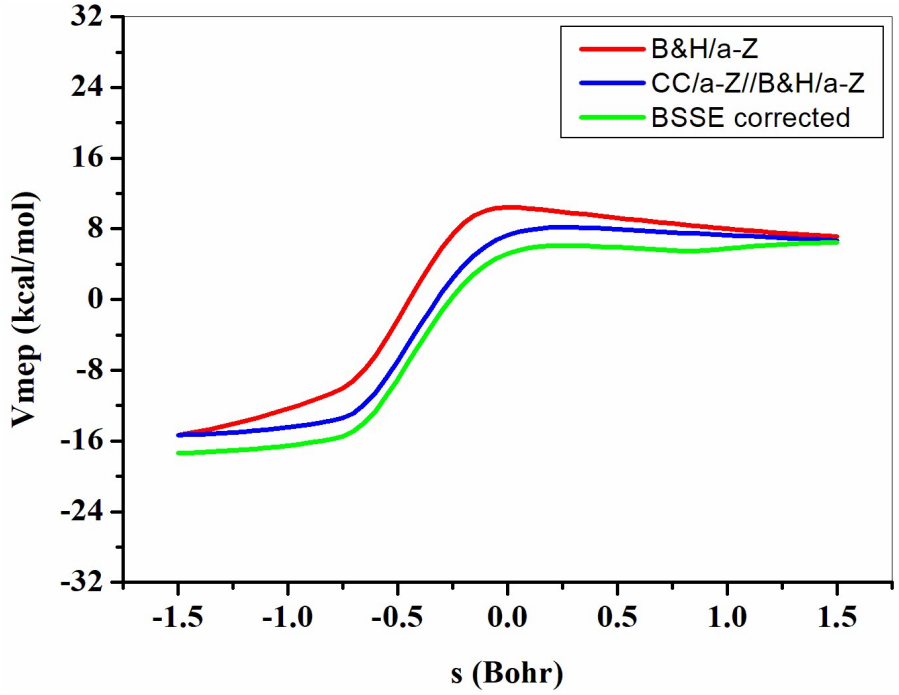


Figure S1-g: Minimum energy pathway (TS7) obtained from CVT/SCT and CVT/SCT/ISPE methodologies using B&H/a-Z, CC/a-Z//B&H/a-Z and CC/a-Z+ BSSE correction //B&H/a-Z.

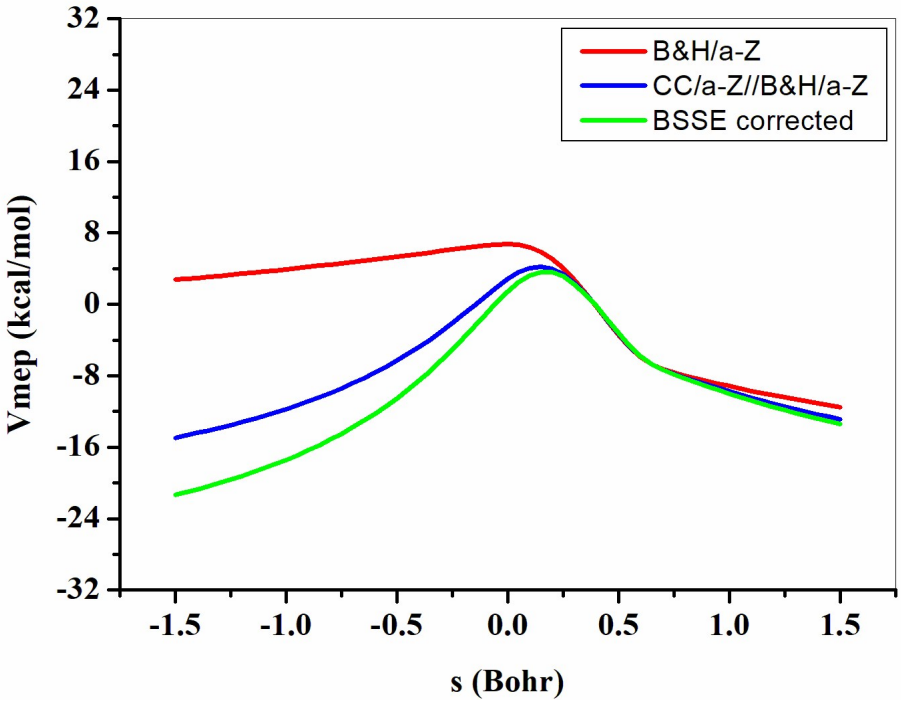
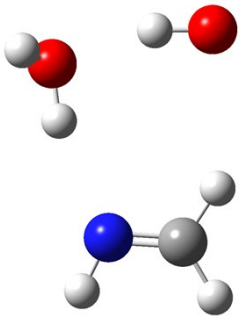


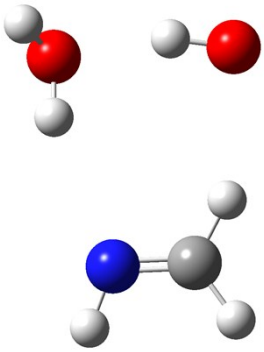
Figure S1-h: Minimum energy pathway (TS8) obtained from CVT/SCT and CVT/SCT/ISPE methodologies using B&H/a-Z, CC/a-Z//B&H/a-Z and CC/a-Z+ BSSE correction //B&H/a-Z.

PRC-1

Initial guess_unoptimized

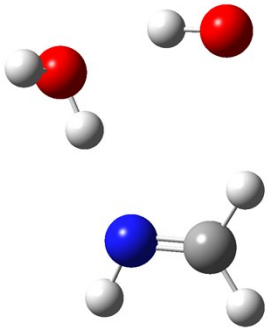


(a)



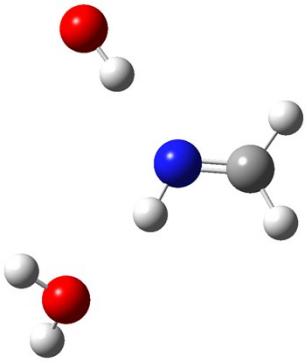
(b)

Final structure_optimized with no imaginary frequency



PRC-2

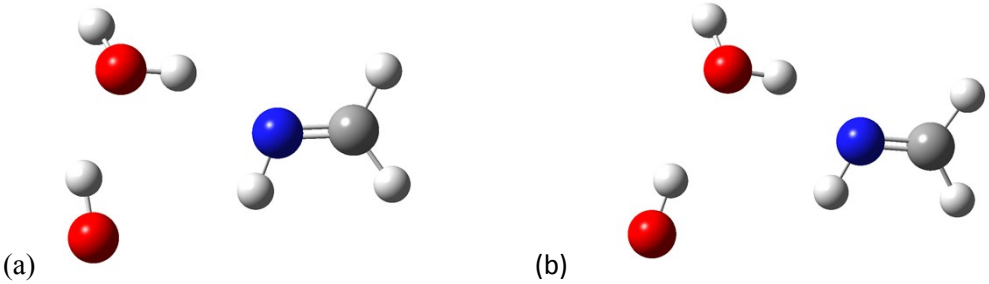
TS with single imaginary frequecny (25*i*)



C	0.54412200	1.84442400	-0.02006800
H	-0.24189300	2.59046700	-0.03347900
H	1.56121200	2.20742700	-0.05793800
N	0.32863100	0.61311200	0.03514800
H	-0.65531600	0.38275500	0.06537900
O	2.20093100	-1.54989500	0.00655600
H	1.57606000	-0.79672000	0.02561100
O	-2.50067800	-0.63253200	-0.05129200
H	-3.11485700	-0.79927400	0.65494000
H	-2.29238000	-1.48356400	-0.42226200

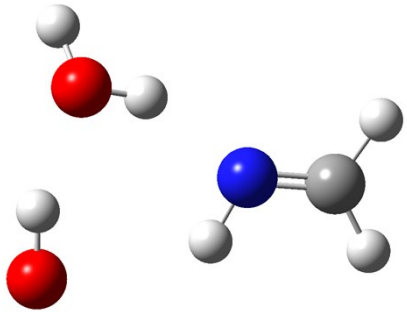
PRC-3

Initial guess_unoptimized



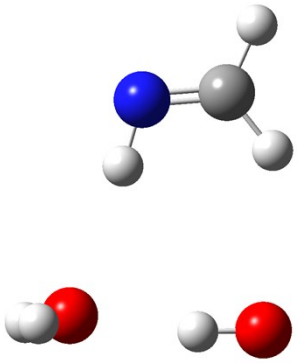
(a) (b)

Final structure_optimized with no imaginary frequency



PRC-4

TS with single imaginary frequecny (~40*i*)



C	2.03139400	0.32227800	0.00000600
H	3.09963200	0.49568400	0.00024400
H	1.39171500	1.19722900	-0.00021200
N	1.60661100	-0.85663900	0.00000500
O	-1.71634800	-1.05965900	0.00002200
H	-1.96618900	-1.57112800	0.76177800
H	-1.96693200	-1.57101500	-0.76156500
O	-1.17588200	1.75465500	-0.00003600
H	-1.45130200	0.82591600	0.00002900
H	0.59627300	-0.87384700	-0.00023400

Figure S2: Transition state of backward reaction of PRCs. These structures were optimized using keyword : OPT=TS, CALCFC