

In silico study on the mechanism of formation of hydrazine and nitrogen in the reactions of excess hydroxylamine with 2,4-dinitrophenyl diethyl phosphate

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Supporting information

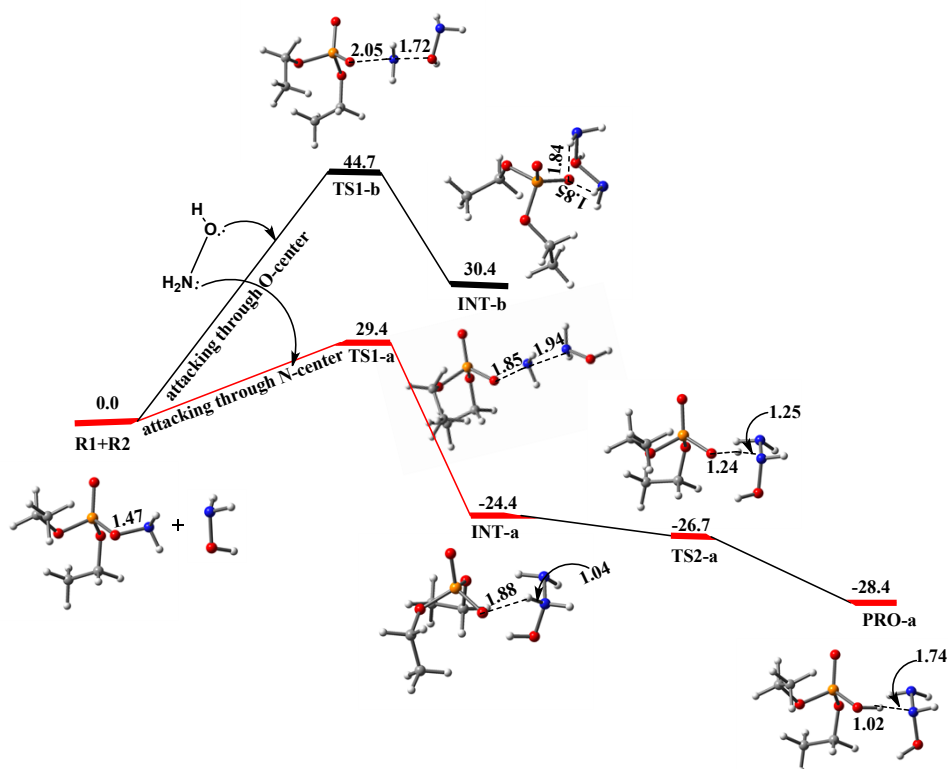


Fig. S1. The potential energy surface and the corresponding geometries for nucleophilic addition in excess of hydroxylamine with hydroxylamine-O-phosphate ester in the phosphate ester intermediate decomposition at MP2/6-31G(d) level in aqueous phase. The relative free energies are given in kcal/mol. (red = oxygen; white = hydrogen; blue = nitrogen; gray = carbon; orange = phosphorous).

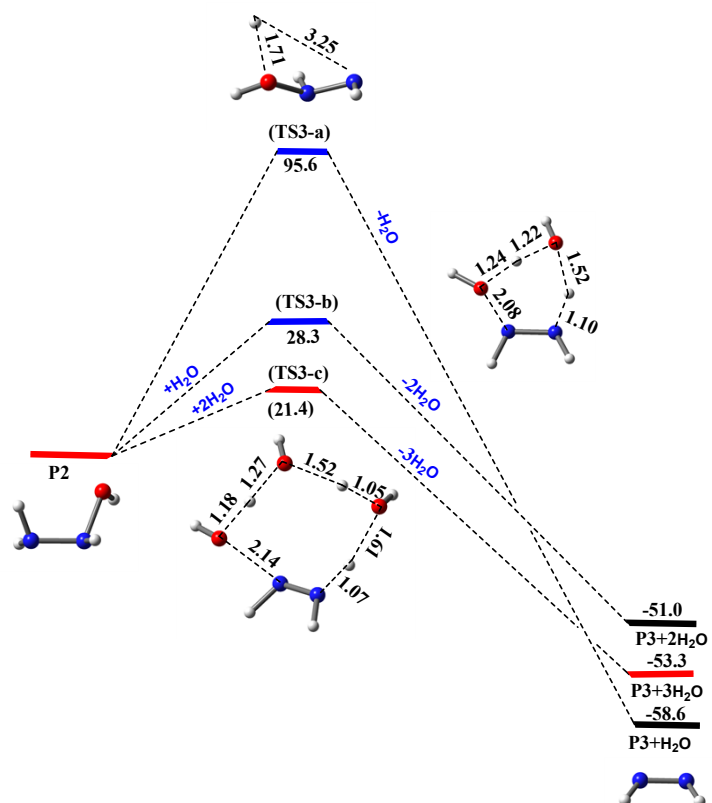


Fig.S2. The potential energy surface and the corresponding geometries for formation of diimide from hydroxylhydrazine in excess of hydroxylamine in the phosphate ester intermediate decomposition at MP2/6-31G(d) level in aqueous phase. The relative free energies are given in kcal/mol. (red = oxygen; white = hydrogen; blue = nitrogen).

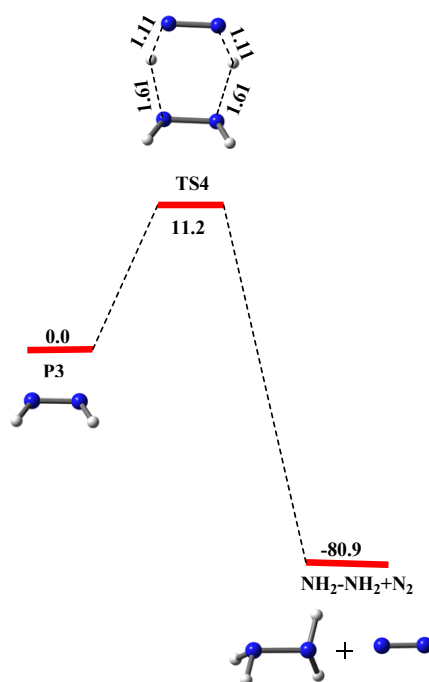


Fig. S3. The potential energy surface and the corresponding geometries for formation of final products (nitrogen and hydrazine) from diimide at MP2/6-31G(d) level of theory in aqueous phase. The relative free energies are given in kcal/mol. (white = hydrogen; blue = nitrogen).

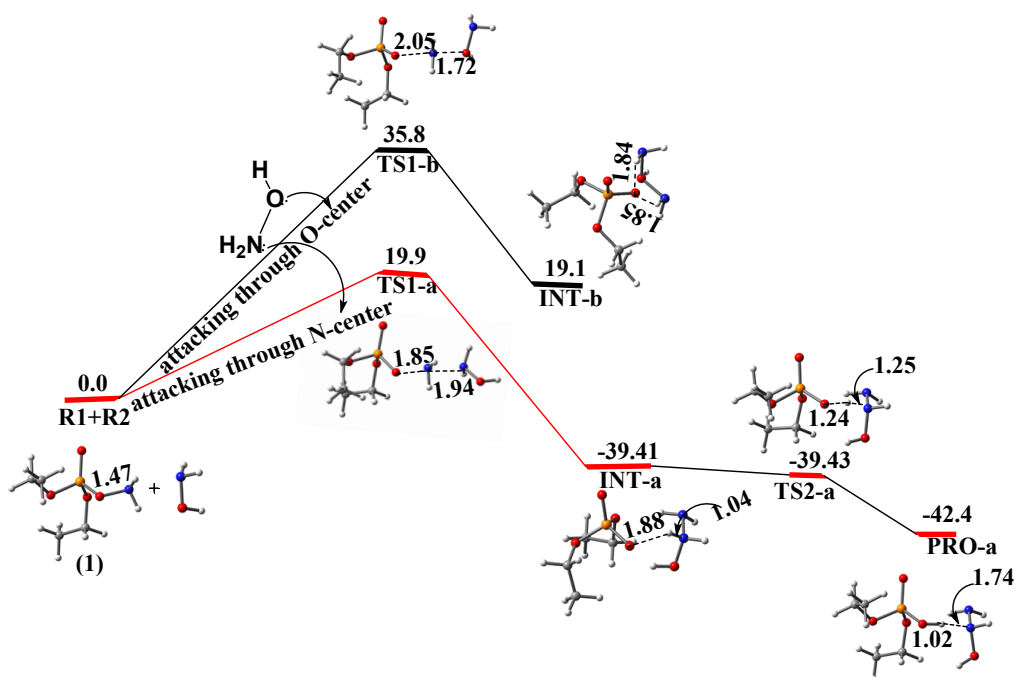


Fig. S4. The potential energy surface and the corresponding geometries for nucleophilic addition in excess of hydroxylamine with hydroxylamine-*O*-phosphate ester in the phosphate ester intermediate decomposition at MP2/6-311++G(d,p)//MP2/6-31G(d) level in the aqueous phase. The relative electronic energies are given in kcal/mol. (red = oxygen; white = hydrogen; blue = nitrogen; gray = carbon; orange = phosphorous).

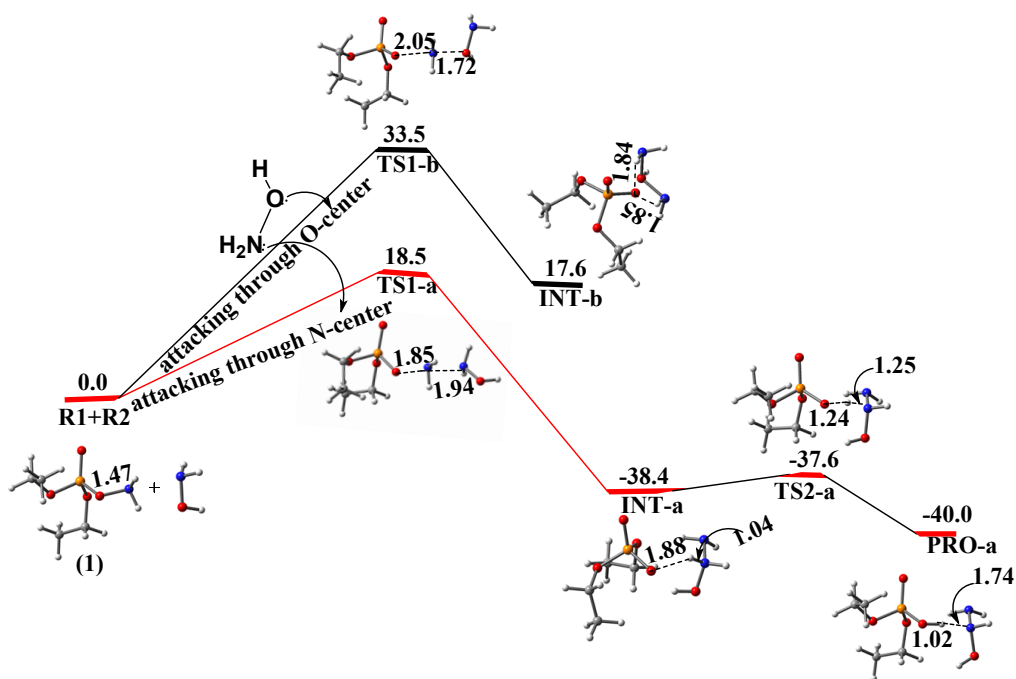


Fig. S5. The potential energy surface and the corresponding geometries for nucleophilic addition in excess of hydroxylamine with hydroxylamine-*O*-phosphate ester in the phosphate ester intermediate decomposition at M06-2x/6-31G(d) level in the aqueous phase. The relative electronic energies are given in kcal/mol. (red = oxygen; white = hydrogen; blue = nitrogen; gray = carbon; orange = phosphorous).

Table S2. Calculated Softness, Fukui function and difference in local softness of nucleophile ($f^-(r)$) (oxygen of hydroxylamine) and electrophiles ($f^+(r)$) (hydroxylamine-*O*-phosphate ester nitrogen and phosphorus centres) in aqueous phase at MP2/6-31G(d) level of theory.

	Global softness	Fukui function	Local softness	Difference in local softness (Δs)
Hydroxylamine (oxygen)	1.53	-0.083 ($f^-(r)$)	-0.13	
Hydroxylamine- <i>O</i> -phosphate ester (nitrogen)	1.51	-0.37 ($f^+(r)$)	-0.56	0.43
Hydroxylamine- <i>O</i> -phosphate ester (phosphorous)	1.51	-0.03 ($f^+(r)$)	-0.04	0.09

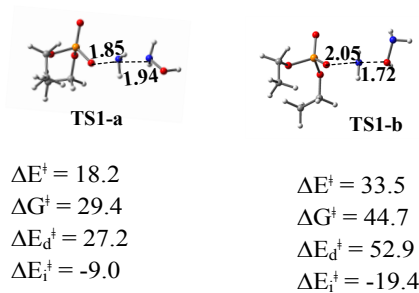


Fig. S6. MP2/6-31G(d) level calculated activation ΔE^\ddagger , ΔG^\ddagger , distortion ΔE_d^\ddagger and interaction energies ΔE_i^\ddagger (kcal/mol) for the reaction between hydroxylamine-O-phosphate ester and hydroxylamine. All distances in the TS are in angstroms.

Cartesian coordinates

R1

$\Delta E = -131.32741146$ Ha

$\Delta G = -131.309030$ Ha

0 1

N	0.70387300	-0.00022800	-0.12209500
H	0.99515400	0.81642600	0.41899700
O	-0.73863800	-0.00021800	-0.10278200
H	-1.00826200	0.00176500	0.83584600
H	0.99510200	-0.81485000	0.42207800

R2

$\Delta E = -854.63322084$ Ha

$\Delta G = -854.489279$ Ha

0 1

C	-2.71327900	-1.73082100	-0.24510600
C	-2.29628400	-0.30294600	-0.51155100
O	-1.50344900	0.18975500	0.61680000

O	0.72741900	0.76731600	1.75257200
P	0.08184900	0.33683300	0.48694500
O	0.54958000	-1.07049300	-0.12598500
C	1.91214100	-1.54147600	0.12482800
C	2.90808800	-0.84654400	-0.77715900
H	-1.83581500	-2.37690700	-0.18783900
H	-1.71820700	-0.21111700	-1.43394100
H	-3.15316300	0.37001700	-0.56992000
H	2.14246700	-1.39041400	1.18139400
H	1.86286200	-2.61115400	-0.07912000
H	3.89804900	-1.28912400	-0.63254300
H	2.97185500	0.21941200	-0.54849300
H	2.62104800	-0.96699200	-1.82385600
O	0.35092800	1.27320900	-0.82926600
H	-3.35924900	-2.08206300	-1.05515200
H	-3.26717000	-1.79462600	0.69393000
N	-0.16819000	2.61877200	-0.53053600
H	0.66751200	3.19680500	-0.63759000
H	-0.74040700	2.80468000	-1.35634200

TS1-a

$\Delta E = -985.93166993$ Ha

$\Delta G = -985.751396$ Ha

0 1

C	-2.03034800	2.81808800	-0.63217800
C	-0.70745700	2.08378600	-0.64567600
O	-0.48366100	1.45992300	0.64701700
O	-0.28510700	-0.56556800	2.17535200

P	-0.55983700	-0.15346400	0.76362700
O	-2.10851300	-0.38979800	0.29788100
C	-2.51576100	-1.74624900	-0.02764400
C	-2.58345400	-1.91949300	-1.52953500
H	-2.84785800	2.11015200	-0.48539900
H	-0.67605900	1.32651300	-1.43308400
H	0.13072700	2.76894900	-0.79751400
H	-1.82891000	-2.46779200	0.42543600
H	-3.49698600	-1.87988500	0.43396200
H	-2.94877400	-2.92103500	-1.77719200
H	-1.59171900	-1.78467900	-1.96403700
H	-3.26594300	-1.18401100	-1.96234900
O	0.28027200	-0.80627100	-0.38998900
H	-2.17901600	3.34088300	-1.58203800
H	-2.04769700	3.55405000	0.17515300
N	2.00647500	-0.25824600	-0.03434900
H	2.25872500	-1.24785000	0.00345200
H	2.06185400	-0.01165000	-1.02486300
N	3.90065300	0.14650900	0.09344400
H	4.20299700	-0.12009700	1.03353300
O	4.68222900	-0.53614700	-0.87475700
H	5.61238100	-0.27018200	-0.71942400
H	4.00428900	1.15685500	-0.02754400

INT1-a

$\Delta E = -986.02380009$ Ha

$\Delta G = -985.837214$ Ha

0 1

C	-0.97862600	2.94288400	-0.58435100
C	0.02414800	1.81761100	-0.70551800
O	0.25662800	1.22650600	0.60422300
O	-0.36657600	-0.41110000	2.44428000
P	-0.39937800	-0.24611600	0.95465600
O	-1.90815200	-0.01713600	0.36907800
C	-2.62648600	-1.16685600	-0.15286500
C	-2.53631600	-1.19731900	-1.66311500
H	-1.93907200	2.54959600	-0.24825000
H	-0.32043100	1.05327900	-1.40708400
H	0.99491600	2.18478600	-1.04893300
H	-2.23409800	-2.08924800	0.28332000
H	-3.65901400	-1.04213400	0.18129400
H	-3.13761900	-2.02154400	-2.05957900
H	-1.49935100	-1.33858100	-1.97273900
H	-2.91140700	-0.26073000	-2.08303500
O	0.30008000	-1.30072800	0.07787200
H	-1.11346200	3.43091300	-1.55461900
H	-0.62522800	3.68714100	0.13314000
N	3.17839400	0.28921800	0.33183600
H	2.28794200	0.76890600	0.50620300
H	3.72516700	0.84094000	-0.33081300
N	2.84521300	-0.91651800	-0.32108600
H	2.16032400	-1.43091100	0.27425400
O	2.20023900	-0.78016100	-1.57866800
H	1.24540000	-0.90317800	-1.27984500

H 3.69727600 -1.46336500 -0.48759200

TS2-a

$\Delta E = -986.01924489$ Ha

$\Delta G = -985.840850$ Ha

0 1

C -0.10076100 3.23672700 -0.21906700

C 0.63781100 1.93932400 -0.45455000

O 0.42965400 1.05118700 0.68502700

O -0.93432300 -0.76801400 1.86504200

P -0.55086500 -0.24636000 0.51872800

O -1.78476400 0.39112400 -0.32001300

C -3.10824100 -0.18639100 -0.14161600

C -3.24810900 -1.49175700 -0.89670300

H -1.17382000 3.04833200 -0.15815000

H 0.30186100 1.45234500 -1.37389200

H 1.71715700 2.09505100 -0.52049200

H -3.29516600 -0.31671100 0.92679600

H -3.79073800 0.57110300 -0.52993900

H -4.27706900 -1.85523200 -0.81675800

H -2.58167000 -2.25497400 -0.48848800

H -3.01013600 -1.34607500 -1.95272400

O 0.18391300 -1.21102100 -0.47125100

H 0.09192300 3.93078500 -1.04270300

H 0.23515500 3.69893100 0.71186200

N 3.02871000 -0.60987800 0.95980200

H 2.40752700 0.19576900 1.05455300

H 3.98571200 -0.27899500 0.82743000

N	2.62384400	-1.29484100	-0.19538700
H	1.37800100	-1.40881500	-0.20824200
O	2.91092000	-0.57691200	-1.41343000
H	2.01565900	-0.42039300	-1.78489600
H	3.16331000	-2.16101400	-0.26757500

PRO-a

$\Delta E = -986.02385661$ Ha

$\Delta G = -985.843572$ Ha

0 1

C	0.01419100	3.22755100	-0.01339700
C	0.68487500	1.92022100	-0.36395400
O	0.41467600	0.94177900	0.69151100
O	-0.89014100	-1.03645500	1.66140500
P	-0.61135300	-0.27527900	0.41416200
O	-1.87524600	0.44398900	-0.27002400
C	-3.21071000	-0.09886900	-0.03299300
C	-3.45605400	-1.33006000	-0.87753900
H	-1.06865200	3.09578800	0.02052000
H	0.33660200	1.53182200	-1.32427700
H	1.77209000	2.01355000	-0.39950100
H	-3.31964300	-0.30842500	1.03299300
H	-3.88136400	0.71620500	-0.30589900
H	-4.49042500	-1.66201100	-0.74809000
H	-2.79488200	-2.14752400	-0.58040400
H	-3.29026900	-1.10630700	-1.93348800
O	0.02281300	-1.08366700	-0.81412400

H	0.25587700	3.98120000	-0.76863900
H	0.36257900	3.58355200	0.95844600
N	2.89001700	-0.91357100	1.04759200
H	2.34190900	-0.06966100	1.21154800
H	3.87426800	-0.68742700	1.21069100
N	2.70479600	-1.25814300	-0.30459500
H	1.00166500	-1.29545000	-0.64343800
O	3.42484800	-0.32944300	-1.17061300
H	2.72326300	0.01498800	-1.75526300
H	3.21417400	-2.13180200	-0.44654600

TS1-b

$\Delta E = -985.90723214$ Ha

$\Delta G = -985.727113$ Ha

0 1

C	-2.20959300	2.72384700	-0.25667100
C	-0.87940200	2.04364500	-0.50141400
O	-0.44398700	1.37435800	0.70684200
O	0.03420000	-0.69683800	2.08467600
P	-0.43371100	-0.25703500	0.72748500
O	-2.04396600	-0.52222900	0.50678600
C	-2.44634200	-1.79233700	-0.06091200
C	-2.75521500	-1.62964800	-1.53431200
H	-2.96879000	1.97616400	-0.02088000
H	-0.94419300	1.32538700	-1.32322100
H	-0.09981400	2.77055600	-0.74800800
H	-1.66802200	-2.54549500	0.09397200
H	-3.33362600	-2.10300800	0.49729300

H	-3.11690000	-2.57390100	-1.95397700
H	-1.85302400	-1.32558200	-2.06738300
H	-3.52741300	-0.86904300	-1.67516100
O	0.26302300	-0.80534800	-0.53569200
H	-2.52070800	3.27921900	-1.14706700
H	-2.12974200	3.42422700	0.57835200
N	2.16617600	-0.05208700	-0.47951000
H	2.36368000	-1.05451900	-0.53577800
H	1.87252300	0.21685600	-1.42186800
N	4.57883000	-0.62883900	-0.00064200
H	5.53667000	-0.46291400	-0.31804600
O	3.81779300	0.34777500	-0.76592500
H	3.88654200	1.23574200	-0.33828700
H	4.52024300	-0.32645200	0.97520300

INT1-b

$\Delta E = -985.93182275$ Ha

$\Delta G = -985.749914$ Ha

0 1

C	-1.19105100	2.21326300	-1.98342000
C	-0.10036400	1.68736400	-1.07529500
O	-0.57788700	1.67130000	0.29107800
O	-1.41772800	0.49305800	2.36528500
P	-0.79113100	0.22510300	1.02617900
O	-1.86015100	-0.43929800	-0.03653200
C	-1.91539700	-1.88195100	-0.13330500
C	-1.34332400	-2.32235700	-1.46387100
H	-2.05164400	1.54253100	-1.95090700

H	0.21456600	0.68492500	-1.37751200
H	0.78012200	2.33696100	-1.09105300
H	-1.37015800	-2.34328500	0.69440000
H	-2.96950900	-2.16014100	-0.04669000
H	-1.43059200	-3.40750800	-1.57752600
H	-0.28871400	-2.04669100	-1.52718200
H	-1.88166500	-1.84199800	-2.28473800
O	0.50890200	-0.58305800	0.95757900
H	-0.82911700	2.27880700	-3.01430200
H	-1.50510900	3.20926400	-1.66180500
N	2.98294200	0.64911800	0.72922900
H	3.59510700	0.02996800	1.27523700
H	2.01292500	0.47409400	1.05357000
N	2.76478300	-1.51289700	-0.39553200
H	1.81204400	-1.50792600	0.01617000
O	2.89816500	-0.02632200	-0.56947000
H	3.78544700	0.11869800	-0.98891100
H	2.64959800	-1.80113800	-1.37549900

P2

$\Delta E = -186.49975289$ Ha

$\Delta G = -186.466009$ Ha

0 1

H	-1.10518600	-0.73458700	-0.86721200
N	-1.19625000	-0.15648500	-0.02687900
H	-1.28627400	-0.79691600	0.75991400
N	-0.00235100	0.57082400	0.18081000
H	0.03495700	1.24088900	-0.58762000

O	1.15535300	-0.26666000	-0.14089500
H	1.50388500	-0.47647800	0.74455900

TS3-a

$\Delta E = -186.34179313$ Ha

$\Delta G = -186.313735$ Ha

0 1

H	1.67305600	1.20745000	1.04878200
N	-1.27518800	0.25467300	0.07843900
H	-1.13058300	1.01717000	-0.60414200
N	-0.20652900	-0.51427400	-0.03647400
H	-0.15689600	-1.21624800	0.71086200
O	1.03310800	0.16769600	-0.14820500
H	1.72157700	-0.53273500	-0.26361500

TS3-b

$\Delta E = -262.67051109$ Ha

$\Delta G = -262.622090$ Ha

0 1

N	0.95850700	-0.91677100	-0.19349100
H	1.39748700	-1.02902300	-1.11400300
H	-0.07554400	-1.26328000	-0.02328800
N	1.14357000	0.14690700	0.47780700
H	1.90552800	0.69608400	0.05836800
O	-0.33047600	1.40366500	-0.28263200
H	-0.49105000	1.92354100	0.52554600
O	-1.49691400	-0.72473400	0.00340700
H	-1.03582500	0.39986100	-0.13126000
H	-1.79601200	-0.76958600	0.92822300

TS3-c

$\Delta E = -338.90012725$ Ha

$\Delta G = -338.830623$ Ha

0 1

N	0.30813800	-1.51037800	-0.29469100
H	0.69268400	-1.95428400	-1.13527600
H	-0.73436500	-1.29789900	-0.20610200
N	1.04575300	-0.96799500	0.56886900
H	2.02945200	-1.15230500	0.34912500
O	1.63436600	0.92872200	-0.23302800
H	2.05760500	1.34479100	0.53891400
O	-2.09977500	-0.46004200	-0.03162000
H	-1.60133600	0.45922800	-0.04813600
H	-2.41006200	-0.55969300	0.88419000
O	-0.69258000	1.67249800	-0.09956600
H	-0.76707700	2.06572000	0.78572400
H	0.51978000	1.31363000	-0.17397900

P3

$\Delta E = -110.32001084$ Ha

$\Delta G = -110.313049$ Ha

0 1

N	-0.60544800	-0.18768500	-0.00000500
H	-1.16933800	0.68002400	0.00003700
N	0.60529400	0.18757800	-0.00000500
H	1.17041400	-0.67927500	0.00003700

P4

$\Delta E = -110.31431807$ Ha

$\Delta G = -110.307813$ Ha

0 1

N	0.63137700	-0.12030700	0.00000600
H	1.02117300	0.84218800	-0.00002700
N	-0.63136700	-0.12031400	-0.00000600
H	-1.02124300	0.84215600	0.00002700

H₂O

$\Delta E = -76.20492572$ Ha

$\Delta G = -76.201197$ Ha

0 1

O	0.00000000	0.00000000	0.12057800
H	0.00000000	0.76017000	-0.48231100
H	0.00000000	-0.76017000	-0.48231100

2H₂O

$\Delta E = -152.41917748$ Ha

$\Delta G = -152.398697$ Ha

0 1

O	1.50660300	-0.08344400	-0.04604200
H	0.52718800	-0.08454400	-0.04964900
H	1.72993400	0.74030800	0.41335800
O	-1.37154000	-0.08414000	-0.05955600
H	-1.65658300	-0.09139800	0.86953200
H	-1.68104000	0.77630400	-0.38845500

3H₂O

$\Delta E = -228.63508979$ Ha

$\Delta G = -228.596728$ Ha

0 1

H	-1.75674500	-1.41369800	0.19880700
O	2.22577600	-0.61803400	-0.08250000
H	2.15441200	-1.00734000	0.80204500
O	-2.10744100	-0.55957700	-0.10530200
H	-0.71309900	0.63550000	-0.09929400
H	-2.74910100	-0.31388600	0.58237000
O	0.07046700	1.23171300	-0.08556300
H	0.05400300	1.62286800	0.80294300
H	1.50011600	0.04374100	-0.09995600

TS4

$\Delta E = -220.62707413$ Ha

$\Delta G = -220.597824$ Ha

0 1

N	1.37463300	0.61240600	0.01866400
H	0.34966500	1.02151300	-0.10687100
N	1.37440800	-0.61237900	0.01827100
H	0.34901800	-1.02112400	-0.10756300
N	-1.22131000	0.65381500	-0.12161000
H	-1.42357600	1.02341400	0.82742800
N	-1.22095100	-0.65392500	-0.12120300
H	-1.42256500	-1.02322000	0.82815800

NH₂-NH₂

$\Delta E = -111.50720291$ Ha

$\Delta G = -111.475114$ Ha

0 1

H	1.03177500	0.40233800	0.83736500
H	-1.03201800	-0.40040300	0.83823300

N	0.71655900	0.10119900	-0.08649700
H	1.12706100	-0.81854300	-0.23202200
N	-0.71652400	-0.10141300	-0.08633900
H	-1.12706300	0.81810900	-0.23372200

N2

$\Delta E = -109.25575727$ Ha

$\Delta G = -109.269288$ Ha

0 1

N	0.00000000	0.00000000	0.56518900
N	0.00000000	0.00000000	-0.56518900

The End