Supporting information for:

Electrochemical Reactivities of Pyridinium in Solution: Consequences for CO_2 Reduction Mechanisms

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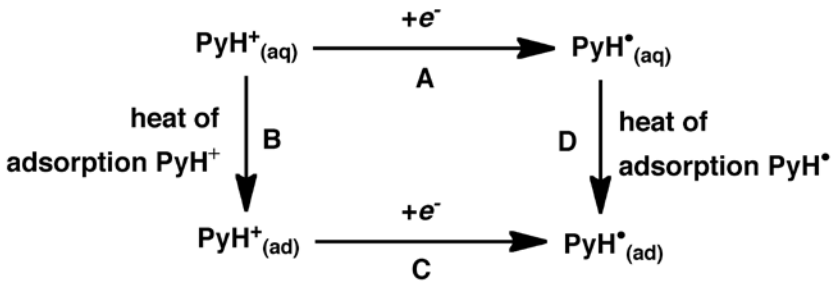
Contents:

Further discussion regarding relative energies of PyH^+ and $PyH^\bullet$

To test the validity of Musgrave and co-workers' assumption that pyridinyl exists in solution we consider the relevant thermodynamic quantities for the key adsorption and electron transfer processes. The most relevant quantity for this discussion, the heat of adsorption of PyH• on the Pt surface, can be derived algebraically using the Born Haber thermodynamic cycle shown in Scheme S1.



Scheme S1. Thermodynamic cycle displaying relative energies of PyH^+ and $PyH^\bullet$.

A, the energy required to add an electron to PyH^+ in solution to form $PyH^\bullet$ in solution was calculated by Musgrave and co-workers to be +1.3 eV. **B**, the energy required to adsorb PyH+ to the Pt(111) surface was also calculated by Musgrave and coworkers to be -1.0 eV. **C**, the energy to add an electron to the adsorbed PyH^+ to form adsorbed $PyH^\bullet$ will be assumed to be the energy based on the reduction observed by the experimental cyclic voltammogram, +0.6 eV. Note that thermodynamic consistency requires that **A + D = B + C**. Solving for **D** thus gives:

D = B + C – A
= (-1.0 eV) + (0.6 eV) – (1.3 eV)
= -1.7 eV

Prof. Musgrave informed us in a private conversation that he believes numerous non-equilibrium effects including concentration dependencies and transport are in play under electrochemical environments, and this simplistic thermodynamic cycle is not a valid representation of the actual chemistry. We disagree with this claim on the basis that even non-equilibrium processes must satisfy the balance of energy given here and that the energy derived here is too great to be accounted for by non-equilibrium effects encountered under these reaction conditions.

Full calculation details and references

Listed energies are in kcal/mol. Calculations are listed as the following:

B3LYP: A gas phase single point (U)DFT-B3LYP/aug-cc-pVDZ calculation at a (U)DFT-B3LYP/aug-cc-pVDZ optimized geometry (using (U)DFT-B3LYP/aug-cc-pVDZ zero-point energies, enthalpies, and entropies)

CCSD(T)-F12: the same calculation above except using (U)CCSD(T)-F12/aug-cc-pVTZ-F12 single point energies.

Unless specified otherwise, all calculations are G_{298} calculations including solvation energies from CPCM(SUAHF) solvation calculations using (U)DFT-B3LYP/aug-cc-pVDZ electron densities with one explicit water.

Electrochemical energies are calculated in a similar manner to those found in the supporting information for reference S1, and additional details regarding acidity and redox potential calculations can be found therein. The following empirical values were used for when counting 1 net electron or proton transfer:

We treat the free energy of 1 H+ in aqueous solution at pH = 0 to be **-270.3 kcal/mol**. This value was attained by adding the free energy of a gas phase proton from the Sackur-Tetrode equation[S2] (-6.3 kcal/mol) to the solvation free energy for a proton, including needed free energy contributions accounting for standard states (-264.0 kcal/mol).[S3,S4] The following energy contribution was used to account for the variation to pH = 0:

$-(0.00008617)(298)\ln 10(n_{H+})pH$

where n_{H+} is the number of protons being transferred between reactant and product.

We treat the free energy of 1 electron referenced to the SCE potential of 0 V to be **-104.3 kcal/mol**. This value comes from the empirically derived value of the standard hydrogen electrode (SHE = 4.281 V[S5]) converted to the saturated calomel electrode reference (SCE = 4.525 V). This value then converted into units of kcal/mol by the relation:

$SCE * 1\ e^- = -G_{298}\ /F$

where F is Faraday's constant, 23.061 kcal/eV.

At different potentials, U, relative to the SCE potential of 0 V, the energy of each transferring electron is then -104.3 kcal/mol + U * F.

References:

[S1] J. A. Keith, E. A. Carter, *J. Am. Chem. Soc.* **2012**, *134*, 7580–7583.
[S2] D. A. McQuarrie, *Statistical Mechanics*, University Science Books, Sausalito, **2000**.
[S3] M. D. Tissandier, K. A. Cowen, W. Y. Feng, E. Gundlach, M. H. Cohen, A. D. Earhart, J. V. Coe, T. R. Tuttle, *J. Phys. Chem. A* **1998**, *102*, 7787–7794.
[S4] J. A. Keith, E. A. Carter, *J. Chem. Theory Comput.* **2012**, *8*, 3187–3206.
[S5] A. A. Isse, A. Gennaro, *J. Phys. Chem. B* **2010**, *114*, 7894–7899.

Cartesian coordinates and energies for molecular species discussed in the text

½ H2
B3LYP Gas G298 -366.8
CCSD(T)-F12 Gas G298 -368.8

H	1.0	0.0000000000	0.0000000000	0.3805815450
H	1.0	0.0000000000	0.0000000000	-0.3805815450

CO_2
B3LYP -118309.2
CCSD(T)-F12 -118218.6

C	6.0	0.0000000000	0.0000000000	0.0000001205
O	8.0	0.0000000000	0.0000000000	-1.1672847651
O	8.0	0.0000000000	0.0000000000	1.1672846445

o-PyH
B3LYP -155650.6
CCSD(T)-F12 -155491.7

H	1.0	0.8660417131	1.2028626543	2.1424433802
C	6.0	0.3225291119	1.2753658900	1.1966862524
C	6.0	-1.0889346394	1.3300246605	1.2122680416
H	1.0	-1.6573186280	1.3020763234	2.1403480068
C	6.0	-1.7369438547	1.4208618797	0.0040084460
H	1.0	-2.8210760789	1.4696961842	-0.0975413006
N	7.0	-0.9993819024	1.4540920812	-1.1460975964
H	1.0	-1.5280720739	1.5217461107	-2.0099771866
C	6.0	0.3649336767	1.4077464426	-1.2892430507
C	6.0	1.0032371682	1.3136528662	-0.0114764123
H	1.0	2.0948193979	1.2698822829	-0.0019565802

p-PyH
B3LYP -155643.0
CCSD(T)-F12 -155483.3

C	6.0	0.3780776197	1.2673029262	1.3070887135
C	6.0	-1.0484882688	1.3301443100	1.1894965714
H	1.0	-1.6698639427	1.3059581021	2.0912325679
C	6.0	-1.7218796543	1.4214643048	-0.0127379957
H	1.0	-2.8068750593	1.4707355972	-0.1204704325
N	7.0	-1.0110763850	1.4555631005	-1.1727844256
C	6.0	0.3488601681	1.4017513434	-1.1740721432
H	1.0	0.8231638198	1.4354551986	-2.1565308340
C	6.0	1.0221455212	1.3109330390	0.0281548652
H	1.0	2.1152021178	1.2711701447	-0.0312105134
H	1.0	-1.5040181915	1.5214470675	-2.0536350404

m-PyH
B3LYP -155643.9
CCSD(T)-F12 -155484.2

H	1.0	0.8246791308	1.2065874437	2.1562194649
C	6.0	0.3336566453	1.2766916634	1.1774636654
C	6.0	-1.0735889609	1.3297843794	1.1854621861
H	1.0	-1.6509244083	1.3012921946	2.1118582620
C	6.0	-1.7468212215	1.4224325761	-0.0206103808
H	1.0	-2.8282670990	1.4716653704	-0.1243067034

N	7.0	-1.0120582562	1.4557242046	-1.1560415736
H	1.0	-1.5021815029	1.5238246435	-2.0448577522
C	6.0	0.3573329690	1.4003014886	-1.1512178194
H	1.0	0.7802813832	1.4369130328	-2.1607919318
C	6.0	1.1382582109	1.3078553786	0.0063375829

Py
B3LYP -155685.4
CCSD(T)-F12 -155527.9

C	6.0	0.0000000000	0.0000000000	-1.4225700383
C	6.0	-1.2001773682	0.0000000000	-0.7082641125
C	6.0	1.2001773682	0.0000000000	-0.7082641125
C	6.0	1.1448165625	0.0000000000	0.6897650940
C	6.0	-1.1448165625	0.0000000000	0.6897650940
N	7.0	0.0000000000	0.0000000000	1.3873204676
H	1.0	-2.0664709009	0.0000000000	1.2775445337
H	1.0	2.0664709009	0.0000000000	1.2775445337
H	1.0	-2.1637044188	0.0000000000	-1.2189936349
H	1.0	2.1637044188	0.0000000000	-1.2189936349
H	1.0	0.0000000000	0.0000000000	-2.5137986029

PyH+
B3LYP -155964.6
CCSD(T)-F12 -155806.1

C	6.0	0.0000000000	0.0000000000	-1.4252687276
C	6.0	1.2132597617	0.0000000000	-0.7253425072
C	6.0	-1.2132597617	0.0000000000	-0.7253425072
C	6.0	-1.1911312497	0.0000000000	0.6605889918
C	6.0	1.1911312497	0.0000000000	0.6605889918
N	7.0	0.0000000000	0.0000000000	1.3024216003
H	1.0	0.0000000000	0.0000000000	2.3204927266
H	1.0	2.0842720154	0.0000000000	1.2824158905
H	1.0	-2.0842720154	0.0000000000	1.2824158905
H	1.0	2.1698496343	0.0000000000	-1.2450742886
H	1.0	-2.1698496343	0.0000000000	-1.2450742886
H	1.0	0.0000000000	0.0000000000	-2.5158537485

Py*-
B3LYP -155725.1
CCSD(T)-F12 -155566.6

C	6.0	0.0000000000	0.0000000000	1.4669744950
C	6.0	0.0000000000	1.2094165382	0.6952030540
C	6.0	0.0000000000	-1.2094165382	0.6952030540
C	6.0	0.0000000000	-1.1545953620	-0.6866478453
C	6.0	0.0000000000	1.1545953620	-0.6866478453
N	7.0	0.0000000000	0.0000000000	-1.4455283284
H	1.0	0.0000000000	2.0928248842	-1.2559137486
H	1.0	0.0000000000	-2.0928248842	-1.2559137486
H	1.0	0.0000000000	2.1901797981	1.1841741652
H	1.0	0.0000000000	-2.1901797981	1.1841741652
H	1.0	0.0000000000	0.0000000000	2.5574112826

PyH*
B3LYP -156033.1
CCSD(T)-F12 -155875.0

H	1.0	0.0024889021	0.0000065810	-3.2926934518
N	7.0	0.0013535683	0.0000003556	-2.2856433153
C	6.0	0.0006865651	-1.2158857839	-1.5915916490
C	6.0	0.0006738795	1.2158860594	-1.5915874580
C	6.0	-0.0006943597	-1.2182394383	-0.2226454875
C	6.0	-0.0007067146	1.2182357901	-0.2226415231
C	6.0	-0.0014524512	-0.0000012917	0.5161461966
H	1.0	-0.0025579257	-0.0000019610	1.6036616877
H	1.0	0.0013187786	-2.1178540540	-2.1984219158
H	1.0	0.0012975888	2.1178554179	-2.1984146380
H	1.0	-0.0011927223	-2.1797997990	0.2913216912
H	1.0	-0.0012151089	2.1797981237	0.2913240165

PyH*_H2O
B3LYP: Gas H0 = -203949.0
B3LYP: Gas G298 = -203972.0
B3LYP: Solv G298 = -203983.7

N	7.0	0.0803860413	-0.0599958454	1.2366468383
C	6.0	-1.1538339403	-0.0946444855	0.5824163593
C	6.0	-1.2112477134	-0.0401503626	-0.7848953759
C	6.0	-0.0230934273	0.0514444189	-1.5673167455
C	6.0	1.2197466251	0.0831679802	-0.8695876725
C	6.0	1.2634019311	0.0282017859	0.4981696483
H	1.0	0.1155655340	-0.1040225547	2.2475420891
H	1.0	2.1866061969	0.0496589260	1.0722976888
H	1.0	-2.0321932476	-0.1656030239	1.2194769469
H	1.0	2.1614019011	0.1519248518	-1.4152835625
H	1.0	-2.1907838902	-0.0688034356	-1.2632698502
H	1.0	-0.0630033537	0.0947367706	-2.6533575863
O	8.0	0.1133401088	-0.2087534021	4.2729773604
H	1.0	-0.0001458545	0.5189757627	4.8960658641
H	1.0	0.0884050889	-1.0118093858	4.8070239980

PyH*_2H2O
B3LYP: Gas H0 = -251887.9
B3LYP: Gas G298 = -251912.1
B3LYP: Solv G298 = -251925.9

C	6.0	1.3272776447	0.3390551046	0.8607887632
N	7.0	0.1882537837	0.6440367733	1.6076884519
C	6.0	-1.0419472047	0.0732616108	1.2534840363
C	6.0	-1.1537723880	-0.6713314618	0.1019644887
C	6.0	-0.0251671087	-0.9240652934	-0.7197087375
C	6.0	1.2323619536	-0.4024829233	-0.2854410714
O	8.0	0.2419809528	0.5004154959	4.5363361277
H	1.0	0.2991195135	0.9585620612	2.5680696277
H	1.0	2.2634742183	0.7498812616	1.2316995438
H	1.0	-1.8875945710	0.3333646630	1.8862284772
H	1.0	2.1397065841	-0.5898658630	-0.8599943101
H	1.0	-2.1366384828	-1.0588461182	-0.1694317343
H	1.0	-0.1085686563	-1.5132338767	-1.6301213195
H	1.0	-0.1027028075	0.7642359728	5.3962746678
H	1.0	-0.0310773199	-0.4303628648	4.4058468425
O	8.0	-0.5701999208	-2.0420504774	3.6102112709
H	1.0	0.0961542219	-2.7301772297	3.4900568801
H	1.0	-0.8010964129	-1.7546338350	2.7084299953

PyH*_3H2O
B3LYP: Gas H0 = -299828.6
B3LYP: Gas G298 = -299855.3
B3LYP: Solv G298 = -299869.3

C	6.0	1.1198945717	-0.3266037688	0.8850645180
N	7.0	0.3692356930	0.5216527316	1.6981705747
C	6.0	-1.0262720061	0.4666040623	1.6563151520
C	6.0	-1.6613130668	-0.3611827913	0.7583818545
C	6.0	-0.9200806502	-1.2002290007	-0.1155591016
C	6.0	0.5050267983	-1.1590540467	-0.0100661092
O	8.0	1.4554928705	1.6463601734	4.1350814675
H	1.0	0.8198861354	1.0362736915	2.4554765681
H	1.0	2.1993377003	-0.2634317092	1.0007341509
H	1.0	-1.5525270955	1.1599212439	2.3083085842
H	1.0	1.1262805214	-1.7939765637	-0.6419836903
H	1.0	-2.7517072471	-0.3476549432	0.7232789424
H	1.0	-1.4175196940	-1.8572770283	-0.8249643640
H	1.0	1.4241589312	2.4998114636	4.5804120224
H	1.0	1.1323888487	0.9848365995	4.7885262724
O	8.0	0.4415041421	-0.3437670813	5.7531744271
H	1.0	-0.1837706082	-0.8505330138	5.1894361864
H	1.0	1.0749358273	-0.9939458227	6.0784538275
O	8.0	-1.2434016566	-1.7038259165	4.0206891011
H	1.0	-1.3105630823	-1.2499527408	3.1591578657
H	1.0	-2.1444773924	-1.9684268215	4.2402402680

PyH*_4H2O
B3LYP: Gas H0 = -347768.1
B3LYP: Gas G298 = -347797.1
B3LYP: Solv G298 = -347812.7

C	6.0	1.1753126166	-0.2351684371	0.8476128248
N	7.0	0.2448630564	-0.0170258979	1.8668408823
C	6.0	-1.1167658580	0.0749824875	1.5657413370
C	6.0	-1.5450898938	-0.0443306987	0.2704773540
C	6.0	-0.6206629517	-0.2652639736	-0.7932056382
C	6.0	0.7599939294	-0.3567769765	-0.4520645434
O	8.0	1.1215033248	0.1415017205	4.7771218365
H	1.0	0.5584886262	0.0722817876	2.8268811228
H	1.0	2.2173165690	-0.2969330938	1.1525021528
H	1.0	-1.7818872663	0.2429043638	2.4095980562
H	1.0	1.5127663264	-0.5254381189	-1.2229058182
H	1.0	-2.6140651071	0.0337942714	0.0690943763
H	1.0	-0.9553989212	-0.3606201793	-1.8235823611
H	1.0	1.8715495467	0.6741408619	5.0651554085
H	1.0	1.2925896067	-0.7787999189	5.1087343249
O	8.0	1.2897105737	-2.3545699610	5.7639660178
H	1.0	0.3804108160	-2.4653241290	6.1326198017
H	1.0	1.4291141238	-3.0983650614	5.1666361286
O	8.0	-1.2611836793	-2.2172778879	6.7372840926
H	1.0	-2.0015315790	-2.7686385681	6.4596848482
H	1.0	-1.4777038794	-1.3044662635	6.4385444238
O	8.0	-1.4789280592	0.3395797013	5.7397305270
H	1.0	-0.5569514296	0.4557756985	5.4220062962
H	1.0	-1.6767712742	1.1103278463	6.2836424512

DHP-
B3LYP -156071.8
CCSD(T)-F12 -155916.7

C	6.0	0.0000024339	-0.2543242888	-1.4539802448
C	6.0	-1.2065527073	-0.0031808964	-0.7167803987
C	6.0	1.2065469857	-0.0031202676	-0.7167825785
C	6.0	1.1958106294	0.0123617480	0.6502075648
C	6.0	-1.1957979088	0.0123060063	0.6502119080
N	7.0	0.0000164708	-0.4632179155	1.3167207242
H	1.0	0.0000143910	-0.1924483521	2.2909620720
H	1.0	-2.0470266391	0.2891737592	1.2757371679
H	1.0	2.0470070422	0.2893367244	1.2757325610
H	1.0	-2.1356168291	0.2622725289	-1.2357882412
H	1.0	2.1355936454	0.2623714668	-1.2358011405
H	1.0	0.0000024897	-0.2239565132	-2.5437493942

p-DHP*+
B3LYP -156304.2
CCSD(T)-F12 -156144.1

C	6.0	-0.0000003396	-0.0002387782	-1.4909512538
C	6.0	1.2469249705	-0.0000975130	-0.6782975193
C	6.0	-1.2469265214	-0.0000835585	-0.6783001212
C	6.0	-1.2080544372	0.0001535322	0.6862189674
C	6.0	1.2080550313	0.0001399712	0.6862217043
N	7.0	-0.0000013265	0.0002581423	1.3370762909
H	1.0	2.0955916444	0.0002484532	1.3155567215
H	1.0	-2.0955897712	0.0002711893	1.3155516548
H	1.0	2.2139257098	-0.0001850370	-1.1805539164
H	1.0	-2.2139340724	-0.0001611428	-1.1805498621
H	1.0	0.0000100752	0.8615404495	-2.1925001848
H	1.0	-0.0000052171	0.0004357070	2.3538545852
H	1.0	-0.0000000034	-0.8622814151	-2.1921770661

o-DHP*+
B3LYP -156305.2
CCSD(T)-F12 -156145.2

C	6.0	-1.2641900657	0.0085843476	-0.7413777643
N	7.0	-0.0833496576	-0.0005845907	-1.3334134696
C	6.0	1.1833253314	-0.0108600508	-0.6057980390
C	6.0	1.0087400016	-0.0110482697	0.8739121695
C	6.0	-0.2294771759	-0.0015552861	1.4634415542
C	6.0	-1.3965241290	0.0086138369	0.6593080867
H	1.0	-2.1349447341	0.0161979822	-1.3979888105
H	1.0	1.7822791208	0.8624966560	-0.9272889890
H	1.0	-2.3923034631	0.0163379030	1.0976372277
H	1.0	1.9183697702	-0.0191381494	1.4753481428
H	1.0	-0.0467444861	0.0005504209	-2.3687619868
H	1.0	-0.3193507783	-0.0018653688	2.5496302895
H	1.0	1.7694229312	-0.8923224496	-0.9288696975
O	8.0	-0.0757804867	0.0060284546	-4.1202370848
H	1.0	-0.0778063267	-0.7623264268	-4.7061388971
H	1.0	-0.0632628520	0.7781569908	-4.7010277318

p-DHP

B3LYP -156409.6
CCSD(T)-F12 -156257.7

C	6.0	0.0000029479	0.0377400669	-1.5300194360
C	6.0	1.2425578819	-0.0535383378	-0.6667583626
C	6.0	-1.2425609528	-0.0534892601	-0.6667652102
C	6.0	-1.1984157776	0.0269319701	0.6742229905
C	6.0	1.1984145195	0.0268950713	0.6742300523
N	7.0	-0.0000010836	0.1928559103	1.3754062313
H	1.0	2.0961480347	-0.0191058287	1.2900028487
H	1.0	-2.0961508580	-0.0190369606	1.2899921561
H	1.0	2.2135188619	-0.1711136917	-1.1485617230
H	1.0	-2.2135306619	-0.1710288824	-1.1485648802
H	1.0	0.0000275823	0.9788204362	-2.1153767526
H	1.0	-0.0000086598	-0.0111595150	2.3630178551
H	1.0	-0.0000060913	-0.7647709787	-2.2896757689

p-DHP_H2O
B3LYP: Gas H0 = -204326.3
B3LYP: Gas G298 = -204349.5
B3LYP: Solv G298 = -204360.1

C	6.0	-0.0128189923	0.0780134874	-1.6057061681
C	6.0	1.2453162899	-0.0044736124	-0.7620455270
C	6.0	-1.2405253820	-0.0541612798	-0.7243224729
C	6.0	-1.1719866075	-0.0467325250	0.6202617174
C	6.0	1.2171055465	0.0011412209	0.5840045406
N	7.0	0.0315863301	0.0617688715	1.3090884734
H	1.0	2.1268575113	-0.0412702305	1.1825130169
H	1.0	-2.0608453974	-0.1255117887	1.2458372226
H	1.0	2.2134516250	-0.0559404663	-1.2611899333
H	1.0	-2.2204295690	-0.1444092462	-1.1941564244
H	1.0	-0.0404789934	1.0295177089	-2.1745655949
H	1.0	0.0498626917	-0.0680341247	2.3118798885
H	1.0	-0.0088413508	-0.7094069667	-2.3825889830
O	8.0	0.0891778266	-0.1905652588	4.3572442146
H	1.0	0.0894845318	0.5740453247	4.9455833121
H	1.0	0.1191655931	-0.9613140402	4.9365122680

p-DHP_2H2O
B3LYP: Gas H0 = -252265.4
B3LYP: Gas G298 = -252289.5
B3LYP: Solv G298 = -252301.4

C	6.0	1.2403479050	-0.5703824031	-0.0473182533
C	6.0	1.2806468057	0.3037526458	0.9752848971
N	7.0	0.1271971335	0.8483160779	1.5485835506
C	6.0	-1.0867594035	0.2399800644	1.2357563011
C	6.0	-1.2203564166	-0.6511840788	0.2307370613
C	6.0	-0.0649401631	-1.0046497177	-0.6851927611
O	8.0	0.1171071892	0.5018777973	4.4883917972
O	8.0	-0.3261176942	-2.0504762433	3.3273167354
H	1.0	0.2118572279	1.1901951314	2.5008126003
H	1.0	2.2183330110	0.6399129272	1.4161520991
H	1.0	-1.9270825626	0.5364985616	1.8628730852
H	1.0	2.1798683563	-0.9473278449	-0.4522135215
H	1.0	-2.2063564651	-1.0718933977	0.0311034760
H	1.0	-0.1956072084	-0.5260685813	-1.6766327218

H	1.0	-0.1341745815	0.5902534971	5.4140841656
H	1.0	-0.0449536334	-0.4336001919	4.2497050537
H	1.0	0.5017194142	-2.5076699601	3.1327153159
H	1.0	-0.6471934171	-1.7505520977	2.4571268860
H	1.0	-0.0529484973	-2.0881501862	-0.8944527668

p-DHP_3H2O
B3LYP: Gas H0 = -300206.1
B3LYP: Gas G298 = -300232.5
B3LYP: Solv G298 = -300244.9

C	6.0	0.5845844972	-1.0813959979	-0.1352260680
C	6.0	0.9646374841	-0.6103697656	1.0625244114
N	7.0	0.0739446698	0.0352170977	1.9451146527
C	6.0	-1.1414545102	0.4797667673	1.3865049139
C	6.0	-1.5992085056	0.0454546029	0.2014240415
C	6.0	-0.8358582808	-0.9526329973	-0.6436920949
O	8.0	1.2311531098	1.5613910909	4.1626668974
O	8.0	0.3432272607	-0.1803136152	6.1094525730
O	8.0	-0.6538942226	-1.7827372233	4.1135338948
H	1.0	0.5049527666	0.6748007403	2.6181684276
H	1.0	1.9833363017	-0.7109869265	1.4349586089
H	1.0	-1.6920618157	1.1942936668	1.9978727360
H	1.0	1.3252738986	-1.5814626446	-0.7599221489
H	1.0	-2.5541104101	0.4266012375	-0.1615789055
H	1.0	-1.3434377754	-1.9377530725	-0.6421250062
H	1.0	1.2182970449	2.4825714881	4.4432791040
H	1.0	0.9695795374	1.0316642534	4.9498861053
H	1.0	-0.0803543926	-0.8217946595	5.4939787643
H	1.0	0.9885891391	-0.6932356293	6.6093222139
H	1.0	-0.4500779246	-1.2497505116	3.3116596456
H	1.0	-1.5691041352	-2.0683756014	4.0125510189
H	1.0	-0.8376577371	-0.6376763003	-1.7017527862

p-DHP_4H2O
B3LYP: Gas H0 = -348146.2
B3LYP: Gas G298 = -348174.6
B3LYP: Solv G298 = -348187.7

C	6.0	0.7974547676	-0.4676985670	-0.2896336160
C	6.0	1.2576305603	-0.1342755992	0.9310103967
N	7.0	0.4169673825	0.2473904507	1.9716714538
C	6.0	-0.9577599517	0.1078873858	1.7969324112
C	6.0	-1.5059440923	-0.2164899886	0.6105601737
C	6.0	-0.6775512430	-0.4320581721	-0.6418545651
O	8.0	1.2509650923	0.3054792344	4.9371776234
O	8.0	1.2667251393	-2.2996361887	5.6205192029
O	8.0	-1.4440253770	-2.2749506067	5.9958508629
O	8.0	-1.4644182959	0.4343161306	5.4822923748
H	1.0	0.7883293425	0.3288754384	2.9101072940
H	1.0	2.3211998426	-0.1426966344	1.1695281742
H	1.0	-1.5578496612	0.2831500557	2.6894370167
H	1.0	1.5172098008	-0.7565354439	-1.0563196636
H	1.0	-2.5908705799	-0.3069202754	0.5464856604
H	1.0	-0.9756988100	-1.3699793804	-1.1462765185
H	1.0	1.9652042901	0.7941139795	5.3612239404
H	1.0	1.3794661480	-0.6471708905	5.1839654067

H	1.0	0.2991524680	-2.4455030109	5.7544320797
H	1.0	1.5486169320	-2.9601653093	4.9772715489
H	1.0	-2.0657439624	-2.7313452410	5.4171845246
H	1.0	-1.5950664990	-1.3142423614	5.8443031127
H	1.0	-0.5002397916	0.5736411326	5.3552480550
H	1.0	-1.7530052916	1.0969311363	6.1198287201
H	1.0	-0.8819042106	0.3623877255	-1.3882146699

o-DHP
B3LYP -156405.7
CCSD(T)-F12 -156253.2

C	6.0	-1.2629447181	0.1654880798	-0.6582510387
N	7.0	-0.0588278764	-0.0691924606	-1.2724562390
C	6.0	1.1807849991	0.2154993480	-0.5454803747
C	6.0	1.0183681029	-0.2186646069	0.8958444401
C	6.0	-0.1986810854	-0.1540698443	1.4787159538
C	6.0	-1.3794561058	0.1880156639	0.6998283536
H	1.0	-2.1259390364	0.2523769852	-1.3200075570
H	1.0	1.4337057980	1.3002430072	-0.5997985179
H	1.0	-2.3510447615	0.3270662963	1.1679113229
H	1.0	1.9036259151	-0.5295781223	1.4519531881
H	1.0	-0.0268046703	-0.0154052914	-2.2831347560
H	1.0	-0.3155507522	-0.4182905742	2.5321092942
H	1.0	2.0024216607	-0.3267401019	-1.0344084410
O	8.0	-0.0483768811	-0.1620570464	-4.3609300459
H	1.0	-0.1586149778	-1.0271801366	-4.7737969409
H	1.0	-0.0342626109	0.4697548045	-5.0897236416

TS-PyH-1
B3LYP: Gas H0 = -322214.5
B3LYP: Gas G298 = -322237.1
B3LYP: Solv G298 = -322248.8

N	7.0	0.1044584959	0.2604095364	0.0062267851
C	6.0	1.3196442413	-0.8323771951	-0.2305307283
H	1.0	0.8384794502	1.2972169074	0.3048365646
O	8.0	0.9914054107	-1.8690980247	-0.7377590181
O	8.0	2.4269098719	-0.3670944163	0.1864758862
H	1.0	2.1328808411	2.5555233563	0.0746282097
O	8.0	1.8234827706	1.8830163925	0.6952563085
H	1.0	2.3273825762	0.8419764151	0.4886648546
C	6.0	-0.6468819246	-0.0879595719	1.1803949669
C	6.0	-2.0083351141	-0.1911491921	1.1693523576
C	6.0	-2.7537301877	0.0324762942	-0.0155029994
C	6.0	-2.0330040104	0.3584451876	-1.1910966758
C	6.0	-0.6706193208	0.4545222734	-1.1839183993
H	1.0	-0.0860257997	0.6756357728	-2.0739480964
H	1.0	-2.5574147615	0.5355590395	-2.1304944389
H	1.0	-3.8377621379	-0.0557899093	-0.0250447561
H	1.0	-2.5126882949	-0.4476558728	2.1013080521
H	1.0	-0.0406609130	-0.2476466523	2.0692444635

TS-PyH-2
B3LYP: Gas H0 = -370156.9
B3LYP: Gas G298 = -370181.1
B3LYP: Solv G298 = -370197.4

C	6.0	0.2206861369	-0.5644763770	-0.0408134607
N	7.0	-0.8959799168	-1.4236019201	0.1964892245
C	6.0	-2.1715345124	-0.9394889850	-0.2398162856
C	6.0	-2.2729195329	0.1577148901	-1.0508332166
C	6.0	-1.1284918901	0.9063113919	-1.4295956779
C	6.0	0.1151128355	0.5252897201	-0.8597335849
C	6.0	-0.8770507441	-2.2475406915	1.5350727754
O	8.0	0.1611380952	-2.1679377609	2.1663504209
O	8.0	-1.9292876046	-2.9270740450	1.6631255050
O	8.0	-0.6294519804	-3.5578375983	-1.2047525850
O	8.0	-1.6514612122	-5.1072615211	0.3975642916
H	1.0	-0.7096159693	-2.6005584522	-0.6435412904
H	1.0	-1.8491979490	-4.3555521422	1.0606108023
H	1.0	-1.1407694808	-3.4873781555	-2.0235316421
H	1.0	-1.0522331687	-4.3356687012	-0.5586212499
H	1.0	-1.0832776686	-5.7439537019	0.8499836892
H	1.0	1.1301153662	-0.8670767540	0.4678050914
H	1.0	1.0119088001	1.1180372959	-1.0432097162
H	1.0	-1.2120747170	1.7798654221	-2.0723670000
H	1.0	-3.2677060723	0.4631944430	-1.3773613298
H	1.0	-3.0152298147	-1.5220123573	0.1162612386

TS-PyH-3
B3LYP: Gas H0 = -418099.7
B3LYP: Gas G298 = -418126.4
B3LYP: Solv G298 = -418145.8

N	7.0	0.2439579324	-0.5375480863	-0.0904541721
C	6.0	-1.0051177368	-1.5682264514	0.2118729819
H	1.0	-0.5594531631	0.4357861353	-0.6986778037
O	8.0	-1.2150784485	1.2765053014	-1.1096495429
O	8.0	-1.7191804390	-1.1126971092	1.1222816210
O	8.0	-1.0224780338	-2.5188549741	-0.5406979494
H	1.0	-2.8716900402	0.0447023881	0.7428436529
H	1.0	-0.7610572325	2.1181114042	-0.8418397553
O	8.0	0.4154807179	3.2178575814	-0.2418758996
H	1.0	0.2005530869	3.9767887557	0.3142995764
H	1.0	1.0112931278	2.6598391928	0.2853709986
O	8.0	-3.2997905377	0.8402649186	0.3209518153
H	1.0	-2.1129245885	1.2014454518	-0.6271545999
H	1.0	-4.1365344896	0.5358573210	-0.0503512009
C	6.0	0.7815666478	0.1107628191	1.0619336247
C	6.0	2.1062321649	0.4564419495	1.1442048549
C	6.0	3.0169471650	0.1377317743	0.1019859458
C	6.0	2.5139719618	-0.6259727144	-0.9846888418
C	6.0	1.1951472898	-0.9823249363	-1.0550867879
H	1.0	0.7762097522	-1.6125173071	-1.8332799232
H	1.0	3.1819650138	-0.9676199194	-1.7758776706
H	1.0	4.0689571194	0.4060663832	0.1681559861
H	1.0	2.4545644699	0.9469171401	2.0550005574
H	1.0	0.0568181849	0.2820479065	1.8525085584

TS-PyH-4
B3LYP: Gas H0 = -466041.4
B3LYP: Gas G298 = -466070.9
B3LYP: Solv G298 = -466090.0

H	1.0	-0.3975758921	0.4788163280	-0.3855855477
N	7.0	0.3442782974	-0.5353792930	-0.0897632861
C	6.0	-0.8314942372	-1.6307546243	0.0182920424
O	8.0	-1.4012541652	-1.5847724982	1.1194226243
H	1.0	-3.0799142221	-1.1352196973	1.4274836712
O	8.0	-3.9105497380	-0.6602537015	1.6566054967
H	1.0	-4.6163144842	-1.0977506912	1.1396276521
C	6.0	0.9808005847	-0.2305871792	1.1651711533
C	6.0	2.3389879434	-0.1267703209	1.2820613576
C	6.0	3.1963551547	-0.3212984045	0.1685066048
C	6.0	2.5894817608	-0.6153639020	-1.0794070891
C	6.0	1.2322886920	-0.7259423576	-1.2056093907
H	1.0	0.7323675010	-0.9492830174	-2.1447391837
H	1.0	3.1996588600	-0.7651689187	-1.9739792251
H	1.0	4.2799873731	-0.2449773125	0.2701651582
H	1.0	2.7492734139	0.1098052015	2.2676152444
H	1.0	0.2927372313	-0.0839354466	1.9933195290
H	1.0	-3.5229174416	0.9485145024	1.1536091744
O	8.0	-1.1128149464	1.4086225474	-0.7254172368
O	8.0	0.1287338578	3.7086131253	-1.2251840559
H	1.0	-0.6170862185	2.2647703529	-0.8700995939
H	1.0	-0.2644916595	4.4593161462	-0.7300518590
H	1.0	1.0871193323	3.7552225796	-1.0222251683
O	8.0	-0.9962795679	-2.2774981264	-1.0105630101
O	8.0	-3.1919936621	1.8145556274	0.8035312988
H	1.0	-3.0218361000	2.3721729156	1.5903010068
H	1.0	-1.8872352305	1.5825403135	-0.1001636524

TS-DHP-1
B3LYP: Gas H0 = -322595.7
B3LYP: Gas G298 = -322618.0
B3LYP: Solv G298 = -322624.7

H	1.0	0.1905946286	0.1692916529	-0.1993370763
N	7.0	0.2434693289	-0.1509102588	1.7216144470
C	6.0	1.6763970955	-0.2551348638	1.4015234373
O	8.0	2.0817498573	0.6759754105	0.6513957141
O	8.0	-0.2271140669	0.2832552977	-1.1069529811
H	1.0	0.2992588316	0.9773651568	-1.6107400842
H	1.0	-0.1598768206	-0.5855560078	-1.6138521991
O	8.0	2.2851013959	-1.2556962065	1.8300103197
C	6.0	-0.3264459890	1.1306712699	1.9416497955
C	6.0	-1.5749456538	1.2956834971	2.4067641964
C	6.0	-2.4933124074	0.1364459621	2.7181613238
C	6.0	-1.6958010051	-1.1472619930	2.7678826091
C	6.0	-0.4369049540	-1.2425658577	2.3096015431
H	1.0	0.1431930106	-2.1628598599	2.3514232749
H	1.0	-2.1567538271	-2.0365795387	3.2066814329
H	1.0	-3.3079334664	0.0690330177	1.9677830563
H	1.0	-3.0075989527	0.3067225852	3.6813369552
H	1.0	-1.9343503028	2.3143386679	2.5688493172
H	1.0	0.3347055784	1.9634102837	1.7031706042

TS-DHP-2
B3LYP: Gas H0 = -370537.3
B3LYP: Gas G298 = -370561.2

B3LYP: Solv G298 = -370578.0

H	1.0	-0.5436091225	-2.6811544277	-0.6258532551
N	7.0	-0.7922121512	-1.5061530104	0.1569047700
C	6.0	-0.7506039774	-2.1272214344	1.5546238646
O	8.0	-1.7503452747	-2.8409777407	1.8227323874
O	8.0	-2.0401954926	-4.9928404116	0.2403856263
O	8.0	-0.3932501401	-3.6645537947	-1.1433617528
O	8.0	0.2712095426	-1.9000999881	2.2107913471
C	6.0	-2.1018771019	-1.0745463575	-0.2757007667
C	6.0	-2.3119863756	0.0397883741	-0.9843203833
C	6.0	-1.2200259101	0.9924719458	-1.3898140800
C	6.0	0.1088917359	0.5331848138	-0.8549976605
C	6.0	0.2767933655	-0.5850461927	-0.1417924431
H	1.0	1.2445459897	-0.8986441709	0.2444030656
H	1.0	0.9930270872	1.1441036021	-1.0623430103
H	1.0	-1.4466688417	2.0114981397	-1.0213782033
H	1.0	-1.1798792138	1.0919911232	-2.4918892002
H	1.0	-3.3393172954	0.2654068956	-1.2862531863
H	1.0	-2.9034069738	-1.7536616753	0.0076013231
H	1.0	-2.0482986733	-4.2938111225	0.9447225208
H	1.0	-1.6874173753	-5.8025216912	0.6650214177
H	1.0	-1.0497727754	-4.3265461167	-0.6831152370
H	1.0	-0.6252605657	-3.5928632850	-2.1046255212

TS-DHP-3

B3LYP: Gas H0 = -418479.9

B3LYP: Gas G298 = -418506.2

B3LYP: Solv G298 = -418522.3

H	1.0	1.0806241185	-1.3604829608	-1.1399911729
N	7.0	0.3940330940	-0.9100055475	0.1133252568
C	6.0	1.6760852020	-0.9581447518	0.9329860096
O	8.0	2.0247888584	-2.1354971267	1.2132586947
O	8.0	4.5996525591	-1.8533321307	0.8375852055
O	8.0	4.0176180257	-1.6959970734	-1.6308940873
O	8.0	1.6089455610	-1.7592500981	-2.0043701538
C	6.0	-0.5595584511	-1.9550028349	0.3445709917
C	6.0	-1.8562892744	-1.8302579660	0.0360212276
C	6.0	-2.4489167693	-0.5699446931	-0.5437817412
C	6.0	-1.4565221266	0.5623716818	-0.4465608151
C	6.0	-0.1694643775	0.3841128147	-0.1283764853
O	8.0	2.2461394979	0.1203337115	1.0991132487
H	1.0	0.5511596121	1.1908347240	-0.0319114168
H	1.0	-1.8044300673	1.5800175825	-0.6284975480
H	1.0	-3.3776121656	-0.3082610176	-0.0084794100
H	1.0	-2.7632891359	-0.7289609104	-1.5930221914
H	1.0	-2.5153793769	-2.6753538273	0.2401162018
H	1.0	-0.1237324342	-2.8473308089	0.7851921610
H	1.0	3.6691692261	-2.0581807802	1.1604144415
H	1.0	4.7522686254	-0.9631612914	1.1854991906
H	1.0	4.3110634853	-1.7530479726	-0.6370549387
H	1.0	4.5880425458	-2.2723231360	-2.1523268834
H	1.0	2.7159787540	-1.7629306631	-1.8386531772
H	1.0	1.3030041396	-2.6711864763	-2.1117486265

TS-DHP-4

B3LYP: Gas H0 = -466420.8
B3LYP: Gas G298 = -466450.8
B3LYP: Solv G298 = -466464.9

H	1.0	0.0357007567	0.6414208271	-0.4608019345
N	7.0	0.5064727282	-0.6279016733	-0.0440852085
C	6.0	-0.9136581621	-1.2364868187	0.1412071758
O	8.0	-1.4303461091	-0.9026258579	1.2299180122
O	8.0	-3.9042413366	-0.4322697574	0.3420351883
O	8.0	-2.8985763607	1.7782623436	-0.6601240467
O	8.0	-0.3624872813	1.6446643501	-0.7924443907
O	8.0	0.7577053339	3.6655642714	0.6429875164
O	8.0	-1.3397413400	-1.8444126872	-0.8376586822
C	6.0	1.2435971573	-0.3896551002	1.1617016982
C	6.0	2.5818633600	-0.3867943916	1.2109138051
C	6.0	3.4545705963	-0.6768679926	0.0156748642
C	6.0	2.6156858170	-1.1766944612	-1.1332867599
C	6.0	1.2783838734	-1.1617031262	-1.1290233804
H	1.0	0.6661626591	-1.5418682176	-1.9414300490
H	1.0	3.1213910321	-1.5867754544	-2.0086543971
H	1.0	4.2206856673	-1.4261689584	0.2814678337
H	1.0	4.0316423561	0.2201801087	-0.2796467685
H	1.0	3.0591654083	-0.2011501880	2.1747395829
H	1.0	0.6065197384	-0.2187777772	2.0251361492
H	1.0	-3.0812615682	-0.7113194237	0.8278198924
H	1.0	-3.9850843496	-1.1082285242	-0.3446269014
H	1.0	-3.3342304804	0.9379239845	-0.3089742106
H	1.0	-3.3010226004	2.5069921265	-0.1737923130
H	1.0	-1.3928993726	1.7044526306	-0.7108618602
H	1.0	0.0485646776	2.3710134772	-0.2659498974
H	1.0	1.3857701299	3.4189322120	1.3341401403
H	1.0	1.1524066689	4.4155870781	0.1803769417