

Experimental and Theoretical Insights into the Mechanisms of Sulfate and Sulfamate Ester Hydrolysis and the End-Products of Type I Sulfatase Inactivation by Aryl Sulfamates

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Comparison of Reaction Free Energy Profiles Computed at Different Levels of Theory

We explored the performance of different computational methods for comparing the hydrolytic reactivities of aryl sulfates and sulfamates. First, geometries of the species involved in the uncatalyzed hydrolyses of *p*-nitrophenyl sulfate (**1**) and sulfamate (**2**) anions using OH⁻ as a model nucleophile were computed at the B3LYP/6-31+G(d) level of theory in implicit water (CPCM). Single-point energies were then computed at the SCS-MP2/6-311+G(d,p), B3LYP/aug-cc-pVTZ, and B3LYP-D3/aug-cc-pVTZ levels of theory. The single-point energies were used in conjunction with the B3LYP/6-31+G(d) thermochemical corrections and solvation energy to compute free energies in solution. Separately, geometry optimizations were performed at the B3LYP-D3/aug-cc-pVTZ level. The free energy profiles for S_N1 and S_N2 hydrolysis of **1** and **2** computed with these four methods are depicted in Figure S1; the black line in this figure reproduces the energy profiles shown for the same reactions in Figure 1 of the paper.

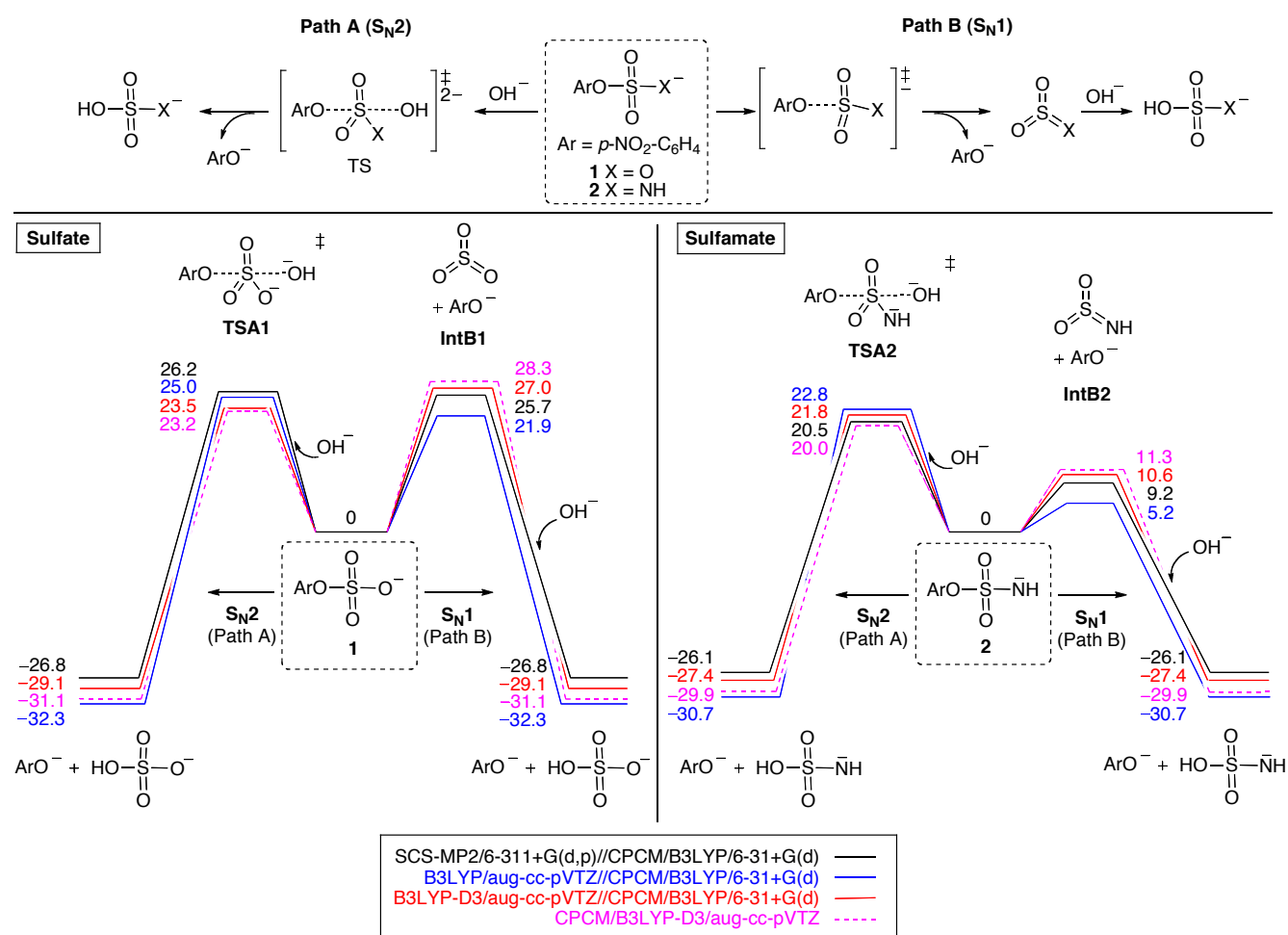


Figure S1. Free energy profiles for hydrolysis of *p*-nitrophenyl sulfate and sulfamate anions, proceeding through S_N1 or S_N2 mechanisms, computed at four different levels of theory. Free energies in water are given in kcal/mol.

The benchmarking calculations lead to the following conclusions:

For a given S_N2 transition state (**TSA1** or **TSA2**), the activation energies predicted by the four methods fall within a range of 3 kcal/mol. The S_N1 barriers (**IntB1**, **IntB2**) are more variable, spanning ranges of ~6 kcal/mol. For sulfate **1**, the barriers for S_N1 and S_N2 mechanisms are close in energy, and some differences in which mechanism is favored are afforded by different methodologies; thus, both SCS-MP2/6-311+G(d,p) and B3LYP/aug-cc-pVTZ predict the S_N1 pathway to be favored, while B3LYP-D3 instead favors the S_N2 pathway. The D3 dispersion correction stabilizes the S_N2 transition state, partially offsetting the large solvation energy penalty. The difference between the two barriers is smallest for SCS-MP2.

Re-optimization of all species with B3LYP-D3/aug-cc-pVTZ generally gave slightly compressed geometries, but the energy profiles obtained from the B3LYP-D3 geometries are very similar to those obtained by performing B3LYP-D3/aug-cc-pVTZ single point calculations on the B3LYP/6-31+G(d) geometries.

With respect to our central question—i.e., the comparison of the reactivities of sulfates and sulfamates in the two hydrolytic mechanisms—all four levels of theory concur on two key points:

- (i) On going from sulfate **1** to sulfamate **2** there is a small (2–6 kcal/mol) decrease in the S_N2 barrier, and
- (ii) On going from sulfate **1** to sulfamate **2** there is a large (16–17 kcal/mol) decrease in the S_N1 barrier, such that S_N1 hydrolysis is consistently predicted to be favored for the sulfamate at all four levels of theory.

Computed Geometries and Energies

In Parts 1 and 2 of the data reported below, geometries were optimized at the B3LYP/6-31+G(d) level in implicit water or diethyl ether (CPCM). Underneath the optimized coordinates are listed the following energies:

B3LYP/6-31+G(d) electronic potential energy in solution (E),
B3LYP/6-31+G(d) zero-point energy in solution (ZPE),
B3LYP/6-31+G(d) enthalpy in solution at 298.15 K (H),
B3LYP/6-31+G(d) free energy in solution at 298.15 K and 1 mol/L (G),
B3LYP/6-31+G(d) single point electronic potential energy in the gas phase (E_{gas})
SCS-MP2/6-311+G(d,p) single-point electronic potential energy in the gas phase ($E_{\text{SCS-MP2}}$)

For selected species, the following energies are also listed:

B3LYP/aug-cc-pVTZ single-point electronic potential energy in the gas phase ($E_{\text{aug-cc-pVTZ}}$)
B3LYP-D3 dispersion energy (E_{disp})

The B3LYP-D3 dispersion energies were calculated with Becke–Johnson damping according to: Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104 and Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456–1465.

In Part 3, geometries were optimized at the B3LYP-D3/aug-cc-pVTZ level in implicit water (CPCM). Underneath the optimized coordinates of these species are listed the following energies:

B3LYP-D3/aug-cc-pVTZ electronic potential energy in solution (E),
B3LYP-D3/aug-cc-pVTZ zero-point energy in solution (ZPE),
B3LYP-D3/aug-cc-pVTZ enthalpy in solution at 298.15 K (H),
B3LYP-D3/aug-cc-pVTZ free energy in solution at 298.15 K and 1 mol/L (G),

Energies are given in Hartree.

PART 1 – Geometries Optimized in Implicit Water at the B3LYP/6-31+G(d) Level

OH⁻

```
H      0.000000      0.000000     -0.864149
O      0.000000      0.000000      0.108019
0 imaginary frequencies
E = -75.929440
ZPE = 0.008471
H = -75.917665
G = -75.940255
Egas = -75.796675
ESCS-MP2 = -75.632793
Eaug-cc-pVTZ = -75.836232
Edisp = -0.000246
```

(*p*-NO₂-C₆H₄O)SO₃⁻ (1)

```
C      0.358718     -1.322913     -0.441993
C     -0.369497     -0.138663     -0.624735
C      0.260130      1.111757     -0.534828
C      1.621217      1.179762     -0.258701
C      2.335983     -0.009755     -0.079139
C      1.721037     -1.263062     -0.169588
```

O	-1.696275	-0.224741	-0.972089
S	-2.901730	0.045282	0.248683
O	-2.633487	-0.997418	1.264941
O	-2.667903	1.431019	0.713584
O	-4.118565	-0.154234	-0.562877
H	-0.320327	2.014761	-0.684724
H	2.126801	2.135120	-0.189127
N	3.764861	0.058653	0.204754
H	2.300538	-2.167030	-0.027979
H	-0.149334	-2.278074	-0.520497
O	4.387538	-0.999970	0.354575
O	4.297497	1.172517	0.284870

0 imaginary frequencies

E = -1135.390494

ZPE = 0.109025

H = -1135.268611

G = -1135.326084

E_{gas} = -1135.308548

E_{SCS-MP2} = -1133.019796

E_{aug-cc-pVTZ} = -1135.631091

E_{disp} = -0.038299

TS: 1 + OH⁻ (TSA1)

C	0.478237	-0.628889	-0.036256
C	0.123747	0.751506	-0.024557
C	1.180185	1.711307	-0.002622
C	2.504481	1.323929	0.008741
C	2.826011	-0.047315	-0.001959
C	1.806374	-1.015453	-0.025166
O	-1.107749	1.210590	-0.034144
S	-2.743608	0.075077	0.001676
O	-2.439355	-0.593362	1.279328
O	-3.600635	1.268936	-0.007170
O	-2.470637	-0.636181	-1.260064
O	-4.973144	-1.217260	0.045913
H	0.914836	2.764234	0.006182
H	3.296070	2.063923	0.026713
N	4.195391	-0.456844	0.011053
H	2.067961	-2.067249	-0.034675
H	-0.298837	-1.381300	-0.056344
H	-4.653547	-2.133553	-0.012640
O	4.464822	-1.674872	0.002274
O	5.087860	0.414662	0.031048

1 imaginary frequency

E = -1211.303604

ZPE = 0.118472

H = -1211.169688

G = -1211.231944

E_{gas} = -1211.021800

E_{SCS-MP2} = -1208.561745

E_{aug-cc-pVTZ} = -1211.378428

E_{disp} = -0.041023

SO₃

S	0.000000	0.000000	0.000000
O	0.000000	1.453878	0.000000
O	1.259096	-0.726939	0.000000
O	-1.259096	-0.726939	0.000000

0 imaginary frequencies

E = -623.778869

ZPE = 0.011526

H = -623.762767
 G = -623.795168
 E_{gas} = -623.772334
 E_{SCS-MP2} = -622.778154
 E_{aug-cc-pVTZ} = -623.923630
 E_{disp} = -0.004385

***p*-NO₂-C₆H₄O⁻**

C	1.228307	1.423195	0.000000
C	0.000001	2.196908	0.000000
C	-1.228306	1.423195	0.000000
C	-1.226532	0.049553	0.000000
C	0.000001	-0.663706	0.000000
C	1.226533	0.049553	0.000000
O	0.000001	3.466092	0.000000
H	-2.168039	1.970386	0.000000
H	-2.158589	-0.504984	0.000000
N	-0.000001	-2.067917	0.000000
H	2.158590	-0.504984	0.000000
H	2.168041	1.970386	0.000000
O	1.094816	-2.691022	0.000000
O	-1.094820	-2.691017	0.000000

0 imaginary frequencies

E = -511.553674
 ZPE = 0.093871
 H = -511.451168
 G = -511.495901
 E_{gas} = -511.474816
 E_{SCS-MP2} = -510.174245
 E_{aug-cc-pVTZ} = -511.646160
 E_{disp} = -0.025819

HSO₄⁻

S	0.139788	0.007003	0.000000
O	-1.536867	0.092124	0.000000
O	0.497817	1.444130	0.000000
O	0.497817	-0.724020	1.243394
O	0.497817	-0.724020	-1.243394
H	-1.889285	-0.817768	0.000000

0 imaginary frequencies

E = -699.821112
 ZPE = 0.025944
 H = -699.789333
 G = -699.826380
 E_{gas} = -699.723624
 E_{SCS-MP2} = -698.558346
 E_{aug-cc-pVTZ} = -699.909868
 E_{disp} = -0.007706

(*p*-NO₂-C₆H₄O)SO₂(NH)⁻ (2)

C	-0.127880	-0.755525	-0.156774
C	0.327204	0.580271	-0.126473
C	-0.611774	1.633158	-0.036671
C	-1.969042	1.365601	0.015886
C	-2.404951	0.032136	-0.013537
C	-1.488586	-1.023835	-0.098468
O	1.619598	0.954882	-0.196882
S	3.003168	-0.192352	0.034644
N	2.816812	-0.902781	1.401953
O	4.067534	0.828095	-0.097234

O	2.838351	-1.130535	-1.095446
H	3.076353	-0.249800	2.145865
H	0.578360	-1.571137	-0.234909
H	-1.844339	-2.046919	-0.124053
N	-3.819210	-0.255544	0.043781
H	-2.689099	2.172144	0.083854
H	-0.248879	2.655627	-0.011507
O	-4.189414	-1.440455	0.020159
O	-4.618084	0.692410	0.114720

0 imaginary frequencies
E = -1115.483016
ZPE = 0.120020
H = -1115.349792
G = -1115.406365
E_{gas} = -1115.404806
E_{SCS-MP2} = -1113.134615
E_{aug-cc-pVTZ} = -1115.719612
E_{disp} = -0.040364

TS: 2 + OH⁻ (TSA2)

C	0.578120	-0.573472	-0.101224
C	0.251649	0.826788	-0.104998
C	1.356551	1.748253	-0.061062
C	2.662455	1.314681	-0.020307
C	2.944239	-0.070314	-0.016948
C	1.887282	-1.004627	-0.060816
O	-0.955392	1.279863	-0.147831
S	-2.880378	0.085195	0.085292
N	-2.704298	-0.349961	1.549108
O	-3.609052	1.338667	-0.113425
O	-2.575267	-0.796888	-1.051985
O	-5.383386	-1.287066	-0.102033
H	1.129810	2.810817	-0.063207
H	3.479897	2.026108	0.011899
N	4.287465	-0.521253	0.026103
H	2.115421	-2.064553	-0.064789
H	-0.224372	-1.299999	-0.157644
H	-2.277973	-1.279636	1.571001
H	-5.023193	-1.721559	-0.892354
O	4.522333	-1.751822	0.035957
O	5.216079	0.319289	0.053826

1 imaginary frequency
E = -1191.396118
ZPE = 0.128664
H = -1191.251044
G = -1191.315249
E_{gas} = -1191.121669
E_{SCS-MP2} = -1188.686331
E_{aug-cc-pVTZ} = -1191.471139
E_{disp} = -0.042121

SO₂NH

S	0.000000	0.022272	0.000000
O	-1.157823	0.911468	0.000000
O	1.352199	0.585387	0.000000
N	-0.303390	-1.473890	0.000000
H	0.568727	-2.013968	0.000000

0 imaginary frequencies
E = -603.894954
ZPE = 0.022752
H = -603.867355

G = -603.901873
 E_{gas} = -603.884903
 E_{SCS-MP2} = -602.909168
 E_{aug-cc-pVTZ} = -604.028706
 E_{disp} = -0.005962

HOSO₂(NH)⁻

O	1.377898	-0.737079	-0.083211
S	-0.114257	0.088157	0.001671
O	-0.023703	0.888092	1.250998
O	-0.022360	0.863368	-1.266604
N	-1.267382	-0.964581	0.124090
H	1.415060	-1.345786	0.677995
H	-1.369961	-1.427696	-0.782824

0 imaginary frequencies
 E = -679.909225
 ZPE = 0.036868
 H = -679.866150
 G = -679.903746
 E_{gas} = -679.810470
 E_{SCS-MP2} = -678.665512
 E_{aug-cc-pVTZ} = -679.989359
 E_{disp} = -0.009575

(PhO)SO₃⁻ (3)

S	-1.877433	0.004387	0.146778
O	-0.588436	-0.070408	-0.979925
O	-1.740920	1.321114	0.815741
O	-3.029136	-0.110465	-0.775490
O	-1.677608	-1.156036	1.048729
C	0.717730	-0.031689	-0.499764
C	1.352723	1.199734	-0.312229
C	2.689450	1.226285	0.097064
C	3.386028	0.031842	0.314060
C	2.741125	-1.194697	0.117473
C	1.403892	-1.231378	-0.289203
H	0.800647	2.117390	-0.487923
H	3.186707	2.181806	0.242467
H	4.425599	0.056635	0.629567
H	3.278497	-2.125610	0.278779
H	0.890585	-2.174641	-0.448175

0 imaginary frequencies
 E = -930.873644
 ZPE = 0.106885
 H = -930.756568
 G = -930.806342
 E_{gas} = -930.781695
 E_{SCS-MP2} = -928.930800

TS: 3 + OH⁻

S	-1.724558	0.144357	0.001258
O	-2.411629	1.454631	0.001496
O	-1.492873	-0.570330	-1.278577
O	-1.487310	-0.565707	1.282411
O	0.012688	1.073344	-0.004556
C	1.200557	0.455792	-0.002555
C	2.358970	1.273943	-0.002225
C	3.638765	0.718881	-0.000186
C	3.816878	-0.671617	0.001708
C	2.680903	-1.488880	0.001329

C	1.391462	-0.946780	-0.000805
H	2.226177	2.353641	-0.003577
H	4.504321	1.378894	0.000037
H	4.813847	-1.104621	0.003446
H	2.793938	-2.571710	0.002753
H	0.530815	-1.603479	-0.001036
O	-3.885813	-0.777381	0.003359
H	-3.681890	-1.726922	-0.038410

1 imaginary frequency
E = -1006.774679
ZPE = 0.116934
H = -1006.645408
G = -1006.698789
E_{gas} = -1006.468046
E_{SCS-MP2} = -1004.449278

PhO⁻

C	0.000000	-1.063421	0.000000
C	-1.211272	-0.290770	0.000000
C	-1.203950	1.104601	0.000000
C	0.000000	1.827723	0.000000
C	1.203950	1.104601	0.000000
C	1.211272	-0.290770	0.000000
H	-2.158329	-0.830204	0.000000
H	-2.153589	1.639726	0.000000
H	0.000000	2.915016	0.000000
H	2.153589	1.639727	0.000000
H	2.158329	-0.830204	0.000000
O	0.000000	-2.360730	0.000000

0 imaginary frequencies
E = -307.012770
ZPE = 0.091140
H = -306.915483
G = -306.953475
E_{gas} = -306.920376
E_{SCS-MP2} = -306.063395

(PhO)SO₂(NH)⁻ (4)

S	1.895769	-0.021197	0.150671
O	0.563941	0.030131	-1.004208
O	3.005180	0.010112	-0.839691
O	1.698570	-1.304242	0.867408
N	1.768582	1.182436	1.135869
H	2.017195	2.036525	0.629916
C	-0.729921	0.014715	-0.517917
C	-1.413082	1.223257	-0.333523
C	-2.745676	1.208490	0.089549
C	-3.396609	-0.006797	0.331132
C	-2.708541	-1.211350	0.142064
C	-1.376614	-1.205326	-0.282389
H	-0.833134	-2.132354	-0.435248
H	-3.209943	-2.159107	0.321721
H	-4.432667	-0.015599	0.659158
H	-3.275092	2.147706	0.229029
H	-0.897612	2.158978	-0.527965

0 imaginary frequencies

E = -910.962771
 ZPE = 0.117623
 H = -910.834483
 G = -910.885486
 E_{gas} = -910.869668
 E_{SCS-MP2} = -909.039685

TS: 4 + OH⁻

S	-1.787154	0.158242	0.027477
O	-2.400089	1.490666	-0.079707
O	-1.755060	-0.756345	-1.133494
N	-1.363377	-0.264405	1.452500
O	0.165655	1.099173	-0.556568
C	1.311091	0.498552	-0.300503
C	2.454066	1.259889	0.081691
C	3.685512	0.654938	0.337356
C	3.839470	-0.736227	0.242476
C	2.727346	-1.505823	-0.124921
C	1.491156	-0.912176	-0.391737
H	2.345392	2.340016	0.163006
H	4.534724	1.275429	0.620311
H	4.798547	-1.205646	0.446718
H	2.823497	-2.587590	-0.209310
H	0.648905	-1.526601	-0.696319
O	-4.108753	-0.842383	0.402862
H	-1.048386	-1.236150	1.419451
H	-4.230440	-1.224310	-0.481906

1 imaginary frequency

E = -986.862396
 ZPE = 0.126267
 H = -986.722522
 G = -986.779421
 E_{gas} = -986.563248
 E_{SCS-MP2} = -984.569910

(PhO)SO(NH)₂⁻

C	1.362533	1.188316	-0.365471
C	0.737091	-0.055069	-0.549419
C	1.446482	-1.236769	-0.283393
C	2.770451	-1.172909	0.159269
C	3.394377	0.066424	0.348053
C	2.685967	1.244160	0.082969
O	-0.542668	-0.121756	-1.039618
S	-1.918707	0.010255	0.152955
N	-1.722112	-1.177331	1.155497
O	-3.001213	-0.059401	-0.866939
N	-1.867234	1.410329	0.839504
H	-1.674922	-2.052203	0.625083
H	0.809085	2.096410	-0.583927
H	3.165653	2.210394	0.219515
H	4.424106	0.113207	0.692580
H	3.315464	-2.092697	0.357451
H	0.954991	-2.193444	-0.435393
H	-1.200004	1.367587	1.612819

0 imaginary frequencies

E = -891.051585
 ZPE = 0.128294
 H = -890.912160
 G = -890.963583
 E_{gas} = -890.958434
 E_{SCS-MP2} = -889.150377

SO(NH)₂

O	0.000000	0.000000	1.488939
S	0.000000	0.000000	0.012248
N	0.000000	1.279359	-0.833697
N	0.000000	-1.279359	-0.833697
H	0.000000	2.096653	-0.217858
H	0.000000	-2.096653	-0.217858

0 imaginary frequencies

E = -584.004861

ZPE = 0.033733

H = -583.965849

G = -584.000411

E_{gas} = -583.993082

E_{SCS-MP2} = -583.036751

(PhO)SO₂(NMe)⁻ (5)

S	1.660268	-0.473714	0.154675
O	1.222740	-1.534080	1.095241
O	2.715017	-0.860191	-0.822158
O	0.316892	-0.366101	-1.007739
N	1.814125	0.889633	0.886645
C	-0.952240	-0.131570	-0.520338
C	-1.416953	1.181847	-0.370761
C	-2.729362	1.410114	0.054917
C	-3.579867	0.334209	0.333369
C	-3.111227	-0.976298	0.180195
C	-1.800588	-1.212473	-0.244131
H	-0.751637	2.010184	-0.594242
H	-3.086961	2.430704	0.166916
H	-4.599551	0.514838	0.663160
H	-3.767357	-1.817480	0.389792
H	-1.426248	-2.224062	-0.368443
C	2.380451	1.994282	0.101399
H	1.726795	2.312874	-0.725317
H	3.367814	1.760328	-0.321970
H	2.495505	2.846918	0.778140

0 imaginary frequencies

E = -950.266484

ZPE = 0.145966

H = -950.108291

G = -950.161976

E_{gas} = -950.175445

E_{SCS-MP2} = -948.222855

SO₂(NMe)

C	0.045019	-2.121487	0.000000
N	0.764578	-0.835209	0.000000
S	0.000000	0.479909	0.000000
O	-1.467259	0.578106	0.000000
O	0.803686	1.705034	0.000000
H	-1.043336	-2.023695	0.000000
H	0.364878	-2.672296	0.888994
H	0.364878	-2.672296	-0.888994

0 imaginary frequencies

E = -643.205229

ZPE = 0.050831

H = -643.147667

G = -643.187764

E_{gas} = -643.196219

E_{SCS-MP2} = -642.095622

(PhO)SO₂(NPh)⁻ (6)

S	0.082854	1.704781	0.196175
O	1.091241	2.295150	1.103033
O	1.012364	0.795952	-0.968899
O	-0.583098	2.641447	-0.740862
N	-0.824544	0.716374	1.009433
C	1.919380	-0.145768	-0.506231
C	3.263803	0.212715	-0.357104
C	4.195509	-0.753314	0.033784
C	3.787628	-2.070089	0.277807
C	2.441000	-2.419216	0.125227
C	1.502200	-1.459886	-0.267087
H	3.565608	1.237331	-0.551872
H	5.240692	-0.476463	0.145764
H	4.514458	-2.819097	0.580551
H	2.118557	-3.441083	0.308234
H	0.455904	-1.719337	-0.395153
C	-1.908362	0.030958	0.437673
C	-2.214437	-0.072275	-0.938245
C	-3.318735	-0.814284	-1.369656
C	-4.146956	-1.474944	-0.457291
C	-3.850381	-1.383086	0.909171
C	-2.751958	-0.645620	1.348833
H	-1.591561	0.427373	-1.671624
H	-3.528030	-0.874454	-2.435686
H	-5.003113	-2.049267	-0.801153
H	-4.478817	-1.888932	1.638954
H	-2.523753	-0.578712	2.409687

0 imaginary frequencies

E = -1142.022163

ZPE = 0.198638

H = -1141.808350

G = -1141.870268

E_{gas} = -1141.938043

E_{SCS-MP2} = -1139.429803

SO₂(NPh)

C	-0.960124	1.012331	-0.143984
C	-0.565374	-0.334486	-0.057634
C	-1.534536	-1.346453	0.064916
C	-2.887202	-1.012829	0.110619
C	-3.284081	0.326357	0.028544
C	-2.318091	1.330494	-0.100497
N	0.764848	-0.817062	-0.124322
S	2.048411	-0.008240	0.029946
O	2.104178	1.447804	0.238536
O	3.294594	-0.770016	-0.113732
H	-1.211394	-2.381157	0.122418
H	-3.629755	-1.799649	0.208233
H	-4.338267	0.586187	0.062890
H	-2.620776	2.371607	-0.169012
H	-0.222059	1.799507	-0.243624

0 imaginary frequencies

E = -834.953340

ZPE = 0.103552

H = -834.840312

G = -834.887719

E_{gas} = -834.944839

E_{SCS-MP2} = -833.284166

(PhO)SO₂(NC₆H₄OMe)⁻ (7)

S	-1.078778	-1.806069	0.042390
O	-2.278969	-2.285303	0.763916
O	-1.687009	-0.586180	-1.059409
O	-0.508593	-2.732342	-0.967078
N	-0.095567	-1.137089	1.058808
C	-2.454616	0.447835	-0.548729
C	1.160132	-0.622042	0.679634
C	-1.841753	1.570527	0.020262
C	-2.631646	2.637473	0.459823
C	-4.024263	2.588115	0.330235
C	-4.628162	1.463123	-0.243676
C	-3.846884	0.389854	-0.681573
H	-0.760333	1.602018	0.107365
H	-2.155907	3.510544	0.899319
H	-4.633878	3.421227	0.669787
H	-5.708936	1.419669	-0.351819
H	-4.301364	-0.488227	-1.130811
C	1.632331	-0.409675	-0.628675
C	2.901108	0.138485	-0.870459
C	3.731739	0.493104	0.196213
C	3.275707	0.292192	1.508676
C	2.017728	-0.251519	1.741143
H	1.014001	-0.671298	-1.479956
H	3.216885	0.281379	-1.898321
O	4.989121	1.037931	0.066924
H	3.918951	0.568719	2.340171
H	1.673678	-0.399395	2.761641
C	5.485302	1.278503	-1.248389
H	4.843365	1.982781	-1.792282
H	5.569677	0.345002	-1.818774
H	6.476542	1.715592	-1.117946

0 imaginary frequencies

E = -1256.548298

ZPE = 0.231162

H = -1256.299292

G = -1256.367502

E_{gas} = -1256.461094E_{SCS-MP2} = -1253.677093**SO₂(NC₆H₄OMe)**

C	0.101438	0.981000	-0.184676
C	-0.317892	-0.362834	-0.088229
C	0.648483	-1.375304	0.032469
C	2.007385	-1.070539	0.061958
C	2.418365	0.268635	-0.032837
C	1.453432	1.286465	-0.157946
N	-1.647436	-0.824424	-0.154516
S	-2.920695	-0.008545	0.077434
O	-2.952106	1.453323	0.279019
O	3.712259	0.679134	-0.013946
C	4.748555	-0.302088	0.117924
O	-4.181820	-0.740630	-0.120695
H	0.322381	-2.408498	0.100520
H	2.726803	-1.875102	0.156356
H	1.786462	2.317199	-0.233269
H	-0.624778	1.780031	-0.278487
H	5.683385	0.258581	0.112646
H	4.650701	-0.848717	1.062301
H	4.732956	-1.002427	-0.724385

0 imaginary frequencies

E = -949.483410
 ZPE = 0.135932
 H = -949.335294
 G = -949.388800
 E_{gas} = -949.472442
 E_{SCS-MP2} = -947.534335

(PhO)SO₂(NC₆H₄NO₂)⁻ (8)

C	1.805573	-0.222551	1.650638
C	0.920915	-0.689787	0.634885
C	1.383101	-0.636475	-0.712093
C	2.643496	-0.150570	-1.014431
C	3.490059	0.298531	0.011971
C	3.063589	0.260046	1.352851
N	-0.304843	-1.128015	1.077443
S	-1.379269	-1.793895	0.106103
O	-0.871806	-2.809530	-0.838730
O	-2.561758	-2.153088	0.906976
O	-1.900630	-0.594061	-1.005309
C	-2.650657	0.483722	-0.535747
C	-4.045330	0.393701	-0.526574
C	-4.799348	1.502677	-0.132346
C	-4.163086	2.689828	0.248791
C	-2.766111	2.767557	0.231855
C	-2.002662	1.663730	-0.160828
H	-4.523195	-0.532905	-0.828451
H	-5.884239	1.438749	-0.126200
H	-4.752777	3.550397	0.552787
H	-2.267029	3.688606	0.521116
H	-0.918649	1.713376	-0.186402
H	0.746879	-0.980957	-1.517772
H	2.980979	-0.113910	-2.043648
N	4.792881	0.799563	-0.307803
H	3.721904	0.608492	2.139842
H	1.463590	-0.255079	2.680546
O	5.531968	1.191120	0.616559
O	5.153143	0.830842	-1.500844

0 imaginary frequencies

E = -1346.548061
 ZPE = 0.200968
 H = -1346.329370
 G = -1346.397891
 E_{gas} = -1346.472943
 E_{SCS-MP2} = -1343.522662

SO₂(NC₆H₄NO₂)

C	-1.300637	1.067644	-0.106040
C	0.073166	0.857095	-0.133156
C	0.578588	-0.454858	-0.062340
C	-0.304309	-1.548230	0.028364
C	-1.676672	-1.340388	0.058015
C	-2.158241	-0.030629	-0.010219
N	1.938889	-0.826628	-0.110324
S	3.147848	0.096995	0.028231
O	4.448370	-0.562291	-0.085629
O	3.067945	1.547032	0.239662
H	0.101672	-2.552719	0.074793
H	-2.362884	-2.174938	0.130396
N	-3.603218	0.197665	0.018368
H	-1.703530	2.071356	-0.160783
H	0.739747	1.707022	-0.208654

O	-4.012965	1.361909	-0.034906
O	-4.348555	-0.784612	0.094436

0 imaginary frequencies
E = -1039.466359
ZPE = 0.105844
H = -1039.348481
G = -1039.403053
E_{gas} = -1039.452509
E_{SCS-MP2} = -1037.357532

(PhO)SO₂(NCN)⁻ (9)

S	1.447126	-0.801971	0.112528
O	0.209800	-0.441205	-0.989206
O	2.519545	-1.203450	-0.810632
O	0.916497	-1.798022	1.050433
N	1.732319	0.549175	0.943581
C	-1.060145	-0.110788	-0.502414
C	-1.991571	-1.125718	-0.273317
C	-3.282629	-0.782208	0.138114
C	-3.633480	0.561173	0.314935
C	-2.690006	1.566345	0.075384
C	-1.395370	1.234412	-0.335530
H	-1.704308	-2.161959	-0.419581
H	-4.014268	-1.565517	0.316861
H	-4.638813	0.823330	0.633013
H	-2.959822	2.610935	0.204949
H	-0.654177	2.002724	-0.532185
C	2.323578	1.545209	0.313793
N	2.843161	2.498381	-0.142732

0 imaginary frequencies
E = -1003.220050
ZPE = 0.116987
H = -1003.090821
G = -1003.146006
E_{gas} = -1003.135870
E_{SCS-MP2} = -1001.078461

SO₂(NCN)

O	-0.813293	1.961254	0.000000
S	0.000000	0.761310	0.000000
N	-0.819744	-0.558461	0.000000
O	1.454640	0.772642	0.000000
C	-0.185355	-1.734322	0.000000
N	0.245652	-2.819567	0.000000

0 imaginary frequencies
E = -696.116557
ZPE = 0.021421
H = -696.088593
G = -696.127939
E_{gas} = -696.105441
E_{SCS-MP2} = -694.902305

(PhO)SO₂(CH₂)⁻ (10)

C	-3.446281	0.114199	0.298528
C	-2.671024	1.256550	0.064790
C	-1.338186	1.139696	-0.340608
C	-0.765406	-0.131662	-0.509679
C	-1.540742	-1.277648	-0.270790
C	-2.875394	-1.152352	0.125136
O	0.521577	-0.277038	-0.963645

S	1.922163	0.039977	0.186190
C	3.309860	-0.425966	-0.560718
O	1.541139	-0.819829	1.340959
O	1.817647	1.512459	0.381319
H	-4.483529	0.209862	0.608738
H	-3.469284	-2.046249	0.300818
H	-3.107059	2.244693	0.192197
H	-1.088444	-2.256271	-0.406392
H	-0.732329	2.020438	-0.527548
H	3.628308	0.225243	-1.368990
H	3.417856	-1.498982	-0.686895

0 imaginary frequencies
E = -894.887116
ZPE = 0.127480
H = -894.748443
G = -894.800019
E_{gas} = -894.800125
E_{SCS-MP2} = -892.982208

SO₂(CH₂)

O	-1.281310	0.781674	0.000000
S	0.000000	0.054571	0.000000
C	-0.000088	-1.546171	0.000000
O	1.281382	0.781609	0.000000
H	0.956555	-2.051113	0.000000
H	-0.956598	-2.051264	0.000000

0 imaginary frequencies
E = -587.846857
ZPE = 0.033416
H = -587.808207
G = -587.843403
E_{gas} = -587.837709
E_{SCS-MP2} = -586.870751

TS3"

C	-4.194785	0.695256	0.107423
N	-2.914516	0.180293	0.146702
C	-2.983507	-1.147051	0.112597
N	-4.277112	-1.498954	0.051578
C	-5.061023	-0.360750	0.047249
O	-0.716428	1.590558	0.247684
P	0.859390	0.737794	-0.258424
O	0.716070	1.083407	-1.738262
O	0.076156	-0.669914	0.250243
O	1.683127	1.526257	0.789125
O	2.337150	-0.512974	-0.640237
C	3.282035	-0.787533	0.339287
O	4.064491	0.378707	0.662033
C	4.241895	-1.878890	-0.119396
H	2.784174	-1.110324	1.277325
H	4.744754	-1.568561	-1.043477
H	3.695465	-2.808663	-0.313919
H	5.002350	-2.075303	0.646241
H	3.346223	1.050181	0.802735
H	-0.556326	1.923224	1.145563
H	-1.986794	0.752550	0.202028
H	-2.137011	-1.814264	0.130097
H	-4.616906	-2.453013	0.014241
H	-6.137461	-0.405445	0.002723
H	-4.383691	1.757240	0.125408
H	0.703542	-1.378421	0.011790

1 imaginary frequency
 E = -1100.219252
 ZPE = 0.195797
 H = -1100.007368
 G = -1100.070438
 E_{gas} = -1100.057326
 E_{SCS-MP2} = -1097.763284

TS4"

N	-2.210965	0.413578	0.146340
C	-2.221556	-0.912148	-0.248321
C	-3.534945	-1.277990	-0.345681
N	-4.281856	-0.162905	-0.007525
C	-3.460939	0.852472	0.287891
H	-3.763916	1.843811	0.586516
H	-5.293922	-0.112116	0.016869
H	-3.999867	-2.211412	-0.619960
H	-1.279711	-1.434519	-0.415600
H	-1.339009	0.971391	0.311207
O	0.141840	1.760249	0.588124
C	0.845974	2.036531	-0.405560
H	0.475110	1.795722	-1.409933
C	1.987267	3.003735	-0.319465
H	1.569097	4.017364	-0.415660
H	2.489724	2.929038	0.648977
H	2.701048	2.847269	-1.130010
O	2.222561	0.270523	-0.790966
P	1.933043	-1.075128	-0.050546
O	1.558920	-0.597173	1.536391
O	3.169643	-1.971376	0.122386
O	0.679567	-1.800569	-0.592140
H	1.020482	0.216835	1.490529

1 imaginary frequency
 E = -1023.810760
 ZPE = 0.169382
 H = -1023.626256
 G = -1023.687465
 E_{gas} = -1023.627517
 E_{SCS-MP2} = -1021.479944

PART 2 – Geometries Optimized in Implicit Diethyl Ether at the B3LYP/6-31+G(d) Level

H₂O

O	0.000000	0.000000	0.118277
H	0.000000	0.769206	-0.473107
H	0.000000	-0.769206	-0.473107

0 imaginary frequencies
 E = -76.429186
 ZPE = 0.021034
 H = -76.404372
 G = -76.428837
 E_{gas} = -76.422562
 E_{SCS-MP2} = -76.270219

Imidazole

C	1.120633	0.299911	0.000000
N	0.000000	1.103913	0.000000
C	-1.091963	0.288056	0.000000
N	-0.743992	-0.987228	0.000000

C	0.637936	-0.987851	0.000000
H	2.120631	0.707358	0.000000
H	1.201150	-1.911251	0.000000
H	-0.010109	2.115564	0.000000
H	-2.103365	0.670832	0.000000

0 imaginary frequencies
E = -226.235554
ZPE = 0.071367
H = -226.159508
G = -226.193466
E_{gas} = -226.226865
E_{SCS-MP2} = -225.615049

(PhO)SO₃⁻ (3)

S	-1.882309	0.005850	0.151096
O	-0.583756	-0.090364	-0.985379
O	-1.729961	1.333063	0.793494
O	-3.031274	-0.120471	-0.770015
O	-1.671750	-1.142601	1.064307
C	0.714271	-0.041134	-0.505291
C	1.344318	1.193918	-0.316180
C	2.679844	1.230007	0.094831
C	3.385119	0.041065	0.314538
C	2.746823	-1.189367	0.120722
C	1.410633	-1.234826	-0.287261
H	0.782751	2.106290	-0.488594
H	3.169770	2.189506	0.241918
H	4.424142	0.073143	0.632528
H	3.288618	-2.117095	0.288210
H	0.899548	-2.180445	-0.439009

0 imaginary frequencies
E = -930.851998
ZPE = 0.106861
H = -930.734926
G = -930.784755
E_{gas} = -930.782477
E_{SCS-MP2} = -928.931591

(PhO)SO₂(NH)⁻ (4)

S	1.903129	-0.030078	0.152571
O	0.556566	0.113636	-1.003938
O	3.006555	0.064320	-0.837619
O	1.683185	-1.354311	0.776972
N	1.776117	1.113543	1.208274
H	2.062323	1.985689	0.755718
C	-0.729178	0.053746	-0.520054
C	-1.445864	1.241328	-0.318641
C	-2.777537	1.189368	0.103209
C	-3.398697	-0.043774	0.331607
C	-2.678596	-1.227722	0.130580
C	-1.348252	-1.184155	-0.294857
H	-0.778215	-2.094089	-0.451438
H	-3.154621	-2.190150	0.303636
H	-4.433976	-0.082260	0.661198
H	-3.329093	2.114190	0.255846
H	-0.951009	2.191150	-0.498399

0 imaginary frequencies
E = -910.940794
ZPE = 0.117602

H = -910.812518
 G = -910.863599
 E_{gas} = -910.870681
 E_{SCS-MP2} = -909.040724

PhO⁻

C	0.000000	1.067676	0.000000
C	-1.212343	0.290183	0.000000
C	-1.203778	-1.104042	0.000000
C	0.000000	-1.829068	0.000000
C	1.203778	-1.104042	0.000000
C	1.212343	0.290182	0.000000
H	-2.158038	0.831798	0.000000
H	-2.153819	-1.640044	0.000000
H	0.000000	-2.916710	0.000000
H	2.153819	-1.640044	0.000000
H	2.158038	0.831798	0.000000
O	0.000000	2.358485	0.000000

0 imaginary frequencies

E = -306.991007

ZPE = 0.090985

H = -306.893857

G = -306.931880

E_{gas} = -306.920690

E_{SCS-MP2} = -306.063753

PhOH

C	-1.208860	0.234378	0.000000
C	0.000000	0.940320	0.000000
C	1.219318	0.252608	0.000000
C	1.222406	-1.143561	0.000000
C	0.019895	-1.861078	0.000000
C	-1.191982	-1.164090	0.000000
O	0.052814	2.313036	0.000000
H	2.147451	0.817042	0.000000
H	2.171964	-1.672701	0.000000
H	0.028338	-2.947352	0.000000
H	-2.134309	-1.706045	0.000000
H	-2.154704	0.772256	0.000000
H	-0.845914	2.681046	0.000000

0 imaginary frequencies

E = -307.485751

ZPE = 0.104450

H = -307.374828

G = -307.413318

E_{gas} = -307.480301

E_{SCS-MP2} = -306.634741

MeCH(OH)O⁻

C	1.384388	-0.195644	-0.108844
H	2.076096	0.573326	0.259666
H	1.431659	-0.211873	-1.205862
H	1.713217	-1.172069	0.275009
C	-0.049813	0.144183	0.340307
O	-0.873130	-1.059346	-0.075680
H	-0.077772	0.089430	1.460428
O	-0.559295	1.266776	-0.149379
H	-1.691251	-0.629487	-0.377550

0 imaginary frequencies

E = -229.770086

ZPE = 0.069784
 H = -229.694342
 G = -229.730485
 E_{gas} = -229.691061
 E_{SCS-MP2} = -229.126962

EtO⁻

O	1.307882	0.135409	0.000000
C	0.000000	0.531683	0.000000
C	-1.019362	-0.634728	0.000000
H	-2.062278	-0.273577	0.000000
H	-0.270119	1.171307	0.886754
H	-0.270119	1.171307	-0.886754
H	-0.872184	-1.267019	0.887511
H	-0.872184	-1.267019	-0.887511

0 imaginary frequencies

E = -154.520986
 ZPE = 0.065492
 H = -154.450766
 G = -154.483444
 E_{gas} = -154.436923
 E_{SCS-MP2} = -154.019500

TS3

C	2.691823	-1.218099	-0.112044
H	1.880614	-1.620722	-0.764647
C	3.988754	-1.975766	-0.425616
H	4.794443	-1.614072	0.226026
H	4.277835	-1.799529	-1.469105
H	3.868826	-3.057364	-0.273205
O	2.310401	-1.645419	1.264014
H	1.722135	-0.918441	1.546389
O	2.800389	0.115480	-0.212885
S	0.744462	1.256052	-0.070086
O	0.291677	0.445034	-1.227095
O	0.611441	0.683007	1.302640
O	1.546153	2.476836	-0.269592
O	-0.965834	2.171812	0.012907
H	-0.949902	2.667665	0.849909
H	-1.982500	1.062424	0.028702
N	-2.634709	0.179121	-0.024139
C	-2.216340	-1.003329	-0.463147
N	-3.236790	-1.871436	-0.365744
C	-4.342049	-1.221418	0.154008
C	-3.952662	0.071645	0.367803
H	-1.220220	-1.201707	-0.831414
H	-3.191261	-2.847569	-0.631029
H	-5.280408	-1.726001	0.320477
H	-4.501430	0.912492	0.762507

1 imaginary frequency

E = -1156.253520
 ZPE = 0.182668
 H = -1156.054339
 G = -1156.119513
 E_{gas} = -1156.143574
 E_{SCS-MP2} = -1153.812007

TS3'

S	0.907676	-1.155559	0.045979
O	0.455628	-0.200867	1.087170
O	0.810666	-0.756440	-1.378178
O	-0.726411	-2.116921	0.091544
H	-0.705342	-2.706048	-0.682849
O	1.791016	-2.275256	0.418713
O	3.065077	0.183860	0.069089
C	2.876911	1.488576	-0.289500
H	2.025901	1.968191	0.265485
H	2.607119	1.610618	-1.372901
C	4.113706	2.385040	-0.045215
H	3.926254	3.431090	-0.341457
H	4.390175	2.370837	1.018752
H	4.975424	2.013896	-0.618154
H	-1.830594	-1.018060	0.009730
N	-2.502978	-0.171485	0.014568
C	-2.120031	1.054583	0.357913
N	-3.179620	1.869401	0.233210
C	-4.271520	1.140397	-0.204131
C	-3.835539	-0.147745	-0.340903
H	-1.120211	1.313055	0.676794
H	-3.168562	2.862570	0.430521
H	-5.235148	1.593562	-0.373711
H	-4.358619	-1.036294	-0.658009

1 imaginary frequency

E = -1081.003315

ZPE = 0.177818

H = -1080.809772

G = -1080.873040

E_{gas} = -1080.885273

E_{SCS-MP2} = -1078.699015

TS4

C	-2.043097	-0.706101	-0.492167
N	-2.007866	0.552218	0.074889
C	-3.235410	0.908385	0.439039
N	-4.071218	-0.092775	0.119024
C	-3.346625	-1.117778	-0.467776
O	0.110559	2.072952	0.404938
C	1.103784	1.881025	-0.349364
C	2.269230	2.837002	-0.302949
O	2.197282	0.316397	0.312603
S	1.643775	-1.128446	0.102035
O	2.822983	-2.062317	0.073299
O	0.893099	-1.149830	-1.219053
O	0.702420	-1.461228	1.234094
H	0.960968	1.326853	-1.284574
H	1.955610	3.778193	-0.777447
H	2.546101	3.050492	0.734001
H	3.133008	2.440442	-0.840988
H	-1.116304	1.154380	0.205118
H	-3.518091	1.835997	0.911836
H	-5.068907	-0.092210	0.290277
H	-3.815834	-2.029793	-0.800647
H	-1.121412	-1.168310	-0.835277

1 imaginary frequency

E = -1079.866189

ZPE = 0.158028

H = -1079.693844

G = -1079.753319

E_{gas} = -1079.751210
E_{SCS-MP2} = -1077.570269

TS4_N

C	-3.345019	-1.179034	-0.450159
C	-2.049195	-0.743313	-0.447487
N	-2.057542	0.531027	0.083859
C	-3.302245	0.873824	0.401740
N	-4.107191	-0.152674	0.085552
O	0.043191	2.114185	0.432675
C	1.028120	1.949184	-0.329122
C	2.189595	2.907418	-0.280743
O	2.197600	0.347004	0.336010
S	1.709975	-1.116502	0.070101
N	0.746383	-1.640914	1.240502
O	2.964715	-1.949113	-0.091462
O	0.873353	-1.111612	-1.195466
H	0.902831	1.365307	-1.248257
H	1.875441	3.845839	-0.761296
H	2.460458	3.127232	0.756418
H	3.056192	2.509878	-0.812714
H	-1.189621	1.148883	0.222753
H	-3.616767	1.808691	0.838629
H	-5.109484	-0.167146	0.226447
H	-3.786267	-2.109391	-0.770083
H	-1.107051	-1.194832	-0.748339
H	1.324712	-1.684695	2.086010

1 imaginary frequency

E = -1059.948802

ZPE = 0.168665

H = -1059.765176

G = -1059.826031

E_{gas} = -1059.833857

E_{SCS-MP2} = -1057.674502

MeCH(OH)₂

C	-1.408394	-0.045160	-0.081892
H	-1.893959	-0.956224	0.282087
H	-1.470479	-0.034653	-1.177219
H	-1.944425	0.823243	0.312310
C	0.043398	-0.003994	0.362033
O	0.707111	1.189038	-0.028903
H	0.128144	-0.007090	1.454667
O	0.686785	-1.146694	-0.182867
H	1.605550	-1.157067	0.134236
H	0.613981	1.287967	-0.992769

0 imaginary frequencies

E = -230.283328

ZPE = 0.084687

H = -230.192682

G = -230.228670

E_{gas} = -230.276869

E_{SCS-MP2} = -229.726821

Adduct 20

S	1.149625	-0.075061	0.028148
O	1.994131	-0.783353	-0.963209
O	1.242101	-0.533537	1.434046
N	1.149727	1.503348	-0.032238
O	-0.405584	-0.596383	-0.484015

C	-1.505322	-0.028556	0.250548
H	-1.274417	-0.120684	1.320444
C	-2.748925	-0.813481	-0.113934
O	-1.700693	1.330659	-0.084426
H	-0.816868	1.757074	0.034584
H	-3.614167	-0.400440	0.415478
H	-2.629445	-1.864373	0.166805
H	-2.929589	-0.748742	-1.192385
H	1.308233	1.767838	-1.008471

0 imaginary frequencies
E = -833.746698
ZPE = 0.098994
H = -833.638323
G = -833.683946
E_{gas} = -833.677804
E_{SCS-MP2} = -832.139821

Adduct 21

C	-0.003900	1.120758	0.027724
H	-0.002384	0.684035	1.031797
C	0.194213	2.629201	0.064774
H	0.152549	3.036862	-0.951711
H	1.171401	2.862608	0.499771
H	-0.589933	3.099931	0.668196
O	-1.250914	0.867889	-0.609959
O	1.025180	0.515754	-0.753901
S	2.242919	-0.413823	0.039780
S	-2.245259	-0.401138	0.008069
O	-1.428863	-1.634452	-0.100222
O	-3.368729	-0.275385	-0.962493
N	-2.570371	-0.093066	1.511834
H	-3.224644	0.694357	1.522718
O	3.199834	0.588603	0.583615
O	2.746835	-1.162754	-1.146886
N	1.589125	-1.221659	1.205770
H	0.870555	-1.832338	0.804200

0 imaginary frequencies
E = -1437.172510
ZPE = 0.111753
H = -1437.046941
G = -1437.104446
E_{gas} = -1436.958036
E_{SCS-MP2} = -1434.436264

MeNH₂

H	-0.949934	1.168646	0.000000
C	0.051650	0.709121	0.000000
N	0.051650	-0.762042	0.000000
H	-0.450911	-1.111703	0.814271
H	-0.450911	-1.111703	-0.814271
H	0.590155	1.067163	0.883870
H	0.590155	1.067163	-0.883870

0 imaginary frequencies
E = -95.865401
ZPE = 0.064291
H = -95.796765
G = -95.827046
E_{gas} = -95.861314
E_{SCS-MP2} = -95.595100

Adduct 22

S	0.507564	-0.074651	0.003213
N	1.656888	1.000877	0.002442
O	0.407905	-0.968118	-1.195933
O	0.507265	-0.805587	1.308570
N	-0.984034	0.828328	-0.092554
H	-0.943303	1.504791	0.670598
C	-2.215129	0.029465	-0.007115
H	-2.291389	-0.564400	0.915680
H	-2.258746	-0.646046	-0.865161
H	-3.070553	0.712128	-0.059710
H	1.702405	1.396339	-0.940439

0 imaginary frequencies

E = -699.317778

ZPE = 0.078271

H = -699.231801

G = -699.273180

E_{gas} = -699.240838

E_{SCS-MP2} = -697.991940

Adduct 23

S	1.292606	0.014330	0.028953
O	1.555358	-0.374175	1.431175
O	1.534180	1.438224	-0.321730
N	1.788976	-1.080582	-0.958912
N	-0.532218	0.000391	-0.041310
C	-1.368456	1.080037	-0.045352
N	-2.643326	0.720788	-0.022485
C	-2.625516	-0.662228	0.007197
C	-1.331173	-1.125458	-0.000391
H	-0.991399	2.092005	-0.073546
H	-3.541946	-1.238210	0.027062
H	-0.909715	-2.119615	0.008280
H	1.701923	-0.714125	-1.910368

0 imaginary frequencies

E = -829.686475

ZPE = 0.084181

H = -829.593393

G = -829.639416

E_{gas} = -829.620890

E_{SCS-MP2} = -828.031757

Imine N-sulfate 24

O	-1.484248	0.894721	0.000000
S	0.010781	0.919876	0.000000
N	0.597920	-0.733235	0.000000
C	-0.286147	-1.653085	0.000000
H	-1.355807	-1.408696	0.000000
C	0.087850	-3.104274	0.000000
H	1.173431	-3.234738	0.000000
O	0.597920	1.477913	1.249754
O	0.597920	1.477913	-1.249754
H	-0.339263	-3.601081	0.881422
H	-0.339263	-3.601081	-0.881422

0 imaginary frequencies

E = -757.333766

ZPE = 0.071428

H = -757.254099

G = -757.297344

E_{gas} = -757.256852

E_{SCS-MP2} = -755.874769

PART 3 – Geometries Optimized in Implicit Water at the B3LYP-D3/aug-cc-pVTZ Level

OH⁻

H 0.000000 0.000000 -0.856115
O 0.000000 0.000000 0.107014
0 imaginary frequencies
E = -75.964271
ZPE = 0.008641
H = -75.952325
G = -75.974898

(*p*-NO₂-C₆H₄O)SO₃⁻ (1)

C 2.365444 0.034776 -0.000010
C 1.460387 -1.020583 0.000211
C 0.103034 -0.760929 0.000253
C -0.345619 0.564502 0.000012
C 0.577672 1.618416 -0.000278
C 1.930798 1.358096 -0.000255
O -1.646877 0.940647 0.000069
S -2.942242 -0.180070 0.000000
O -2.763102 -0.947353 1.233391
N 3.787382 -0.246838 0.000017
O 4.153041 -1.420929 -0.000642
O 4.571857 0.700330 0.000687
O -4.060401 0.757112 0.000002
O -2.762928 -0.947255 -1.233455
H 0.210744 2.633823 -0.000529
H 2.648225 2.162348 -0.000478
H 1.820756 -2.036444 0.000408
H -0.598515 -1.576814 0.000460
0 imaginary frequencies
E = -1135.753790
ZPE = 0.109527
H = -1135.631588
G = -1135.688417

TS: 1 + OH⁻ (TSA1)

C -0.459083 -0.613932 0.022660
C -0.110753 0.762485 0.032875
C -1.169316 1.711476 0.029651
C -2.483396 1.319509 0.015779
C -2.796866 -0.045224 0.004997
C -1.777692 -1.002743 0.009057
O 1.109873 1.218658 0.046363
S 2.736862 0.068476 -0.022824
O 2.405097 -0.558787 -1.296143
O 3.583652 1.251045 -0.008368
O 2.456171 -0.639429 1.222342
O 4.850579 -1.278264 -0.053681
H -0.910212 2.760544 0.037187
H -3.277089 2.049555 0.012043
N -4.162444 -0.460292 -0.010530
H -2.036842 -2.049657 0.001758
H 0.319715 -1.356861 0.027147
H 4.577653 -1.862016 0.660287
O -4.422182 -1.670948 -0.020784
O -5.051100 0.402155 -0.013433
1 imaginary frequency

E = -1211.699136
 ZPE = 0.119094
 H = -1211.564792
 G = -1211.626356

SO₃

S	0.000000	0.000000	0.000000
O	0.000000	1.439104	0.000000
O	1.246301	-0.719552	0.000000
O	-1.246301	-0.719552	0.000000

0 imaginary frequencies

E = -623.934244

ZPE = 0.011858

H = -623.917861

G = -623.950153

p-NO₂-C₆H₄O⁻

C	1.222084	-1.415836	0.000000
C	0.000000	-2.187757	0.000000
C	-1.222084	-1.415836	0.000000
C	-1.218734	-0.050419	0.000000
C	0.000000	0.659153	0.000000
C	1.218734	-0.050419	0.000000
O	0.000000	-3.449065	0.000000
H	-2.157426	-1.959712	0.000000
H	-2.144475	0.504267	0.000000
N	0.000000	2.061946	0.000000
H	2.144475	0.504267	0.000000
H	2.157426	-1.959712	0.000000
O	1.087624	2.677280	0.000000
O	-1.087624	2.677280	0.000000

0 imaginary frequencies

E = -511.750914

ZPE = 0.093766

H = -511.648558

G = -511.693230

HSO₄⁻

S	0.135788	0.007529	0.000000
O	-1.519752	0.087190	0.000000
O	0.493679	1.429817	0.000000
O	0.493679	-0.714948	1.230994
O	0.493679	-0.714948	-1.230994
H	-1.862885	-0.817357	0.000000

0 imaginary frequencies

E = -700.014826

ZPE = 0.026429

H = -699.982615

G = -700.019576

(*p*-NO₂-C₆H₄O)SO₂(NH)⁻ (2)

C	-0.113597	-0.749748	-0.129691
C	0.336684	0.578936	-0.102294
C	-0.597075	1.625846	-0.027409
C	-1.947298	1.359177	0.015819
C	-2.378753	0.033824	-0.011069
C	-1.467635	-1.015752	-0.083151
O	1.626091	0.952274	-0.157503
S	2.967207	-0.188884	0.023838
N	2.772444	-0.939197	1.355464

O	4.040881	0.803390	-0.070562
O	2.799818	-1.077551	-1.126671
H	3.027493	-0.315968	2.117819
H	0.591478	-1.559751	-0.194567
H	-1.824331	-2.032809	-0.106277
N	-3.794520	-0.254163	0.035147
H	-2.667137	2.159403	0.072957
H	-0.235482	2.643135	-0.004700
O	-4.157878	-1.430295	0.011635
O	-4.584759	0.688177	0.096334

0 imaginary frequencies
E = -1115.838292
ZPE = 0.120386
H = -1115.704853
G = -1115.761197

TS: 2 + OH⁻ (TSA2)

C	0.529614	-0.538884	-0.189723
C	0.216522	0.857014	-0.150218
C	1.323611	1.759921	-0.049867
C	2.615912	1.313552	0.012166
C	2.882765	-0.065021	-0.019117
C	1.825596	-0.980896	-0.122973
O	-0.978573	1.318766	-0.204063
S	-2.830995	0.072086	0.083530
N	-2.507446	-0.453921	1.477670
O	-3.595202	1.300807	0.033854
O	-2.586884	-0.700260	-1.125973
O	-5.227149	-1.314741	0.006818
H	1.108399	2.819087	-0.023948
H	3.436949	2.009153	0.087864
N	4.219722	-0.530477	0.048114
H	2.046123	-2.036416	-0.156358
H	-0.273209	-1.250181	-0.297298
H	-2.052923	-1.359064	1.386246
H	-4.885476	-1.685978	-0.811649
O	4.438114	-1.753661	0.027225
O	5.145443	0.294926	0.126709

1 imaginary frequency
E = -1191.785206
ZPE = 0.129216
H = -1191.639788
G = -1191.704278

SO₂NH

S	0.000000	0.021838	0.000000
O	-1.089308	0.970247	0.000000
O	1.367058	0.501552	0.000000
N	-0.382870	-1.443095	0.000000
H	0.458095	-2.022138	0.000000

0 imaginary frequencies
E = -604.043453
ZPE = 0.023143
H = -604.015532
G = -604.049909

HOSO₂(NH)⁻

O	1.351779	0.744102	0.066468
S	-0.107903	-0.089076	-0.000789
O	-0.020084	-0.897083	-1.227302

O	-0.011344	-0.850068	1.257872
N	-1.259611	0.948133	-0.126261
H	1.339419	1.393302	-0.649861
H	-1.358498	1.419375	0.770002

0 imaginary frequencies
E = -680.096580
ZPE = 0.037333
H = -680.053090
G = -680.090582

Experimental Data

Potassium 4-chlorophenylsulfate

M.p. 310-314 °C; ^1H NMR (400 MHz, D_2O) δ 7.12 (app. d, 2H, Ar), 7.28 (app. d, 2H, Ar). ^{13}C NMR (100 MHz, D_2O) δ 124.1, 130.7, 132.0, 150.8 (Ar). IR (KBr disc) ν 1062 s; 678 m, 630 m, 615 m, 574 s, 549 w (S-O) cm^{-1} .

Potassium phenylsulfate

M.p. 185-186°C (dec); ^1H NMR (400 MHz, D_2O) δ 7.26-7.45 (5 H, m); ^{13}C NMR (100 MHz, D_2O) δ 121.4, 125.9, 130.0, 151.5; IR (KBr) ν 1062, 767, 701, 653, 569 cm^{-1} .

Potassium 3-chlorophenylsulfate

M.p. ??? °C (dec); ^1H NMR (400 MHz, D_2O) δ 7.23-7.26 (1 H, m), 7.32-7.43 (3 H, m); ^{13}C NMR (100 MHz, D_2O) δ 123.7, 125.6, 130.0, 134.5, 137.8, 155.3 ppm; IR (KBr) ν 1593, 1579, 1473, 1298, 1274, 1266, 1237, 1062, 925, 855, 770, 602, 593, 574 cm^{-1} ; Anal. calcd. for $\text{C}_6\text{H}_4\text{ClKO}_4\text{S}$: C, 29.2; H 1.63. Found C, 29.0; H, 1.4%.

Potassium 3-nitrophenylsulfate

M.p. ??? °C (dec); ^1H NMR (400 MHz, D_2O) δ 7.62-7.71 (3 H, m), 8.15-8.18 (2 H, m); ^{13}C NMR (100 MHz, D_2O) δ 120.2, 124.3, 131.6, 133.9, 151.7, 154.7 ppm; IR (KBr) ν 1534, 1358, 1292, 1272, 1249, 1060, 944, 832, 752, 724, 667, 592 cm^{-1} ; Anal. calcd. for $\text{C}_6\text{H}_4\text{KNO}_6\text{S}$: C, 28.0; H 1.6; N, 5.4. Found C, 28.0; H, 1.4; N, 5.2%.