A Theoretical Comparison of *p*-Nitrophenyl Phosphate and Sulfate Hydrolysis in Aqueous Solution: Implications for Enzyme Catalyzed Sulfuryl Transfer

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RELEVANT STATIONARY POINTS FOR *P*-NITROPHENYL PHOSPHATE HYDROLYSIS

PCM/B3LYP/6-31+G Geometry for p-Nitrophenyl Phosphate*

P	-3.037853	-0.191158	0.027174
O	-4.166256	0.842338	-0.056720
O	-1.640281	0.923044	-0.094231
O	-2.845853	-0.858130	1.394413
O	-2.885585	-1.113865	-1.187777
C	-0.355117	0.579211	-0.064836
C	0.593618	1.633433	-0.034095
C	1.950076	1.368044	-0.006973
C	2.390701	0.032500	-0.009019
C	0.110098	-0.759064	-0.071391
C	1.468858	-1.026873	-0.043532
H	-0.606949	-1.568479	-0.116425
H	1.823644	-2.050713	-0.050897
N	3.796321	-0.250266	0.021674
H	2.669827	2.177441	0.017776
H	0.232819	2.657361	-0.031003
O	4.175289	-1.436766	0.024778
O	4.603284	0.698394	0.044575

PCM/B3LYP/6-31+G Optimized Transition State Geometry for p-Nitrophenyl Phosphate Hydrolysis*

O	-3.657203	1.299879	0.150893
P	-2.743976	0.084641	0.158038
O	-4.489926	-1.256894	-0.200991
O	-1.193068	1.095510	-0.041441
O	-2.415054	-0.614557	-1.302079
O	-2.354736	-0.689266	1.404186
H	-5.214316	-0.635072	-0.375207
C	0.058590	0.678729	-0.023088
H	-3.245120	-1.157980	-1.395816
C	1.075283	1.674737	-0.080123
C	2.413614	1.336038	-0.076290
C	2.782893	-0.021369	-0.010995
C	1.799180	-1.025209	0.048470
C	0.458263	-0.684871	0.043051
H	0.772370	2.716369	-0.129318
H	3.176889	2.103800	-0.121259
N	4.165092	-0.380696	-0.003727
H	2.096688	-2.066118	0.098334
H	-0.297087	-1.456740	0.095076
O	4.480830	-1.586365	0.060240
O	5.027611	0.519527	-0.061114

PCM/B3LYP/6-31+G* Structure Obtained from Following the Intrinsic Reaction Coordinate (IRC) on the Optimized Transition State in the Reactant Direction for 50 Steps

O	-3.631176	1.319866	0.158987
P	-2.575658	0.211467	0.138572
O	-4.803557	-1.464614	-0.303174
O	-1.134491	1.172499	-0.038426
O	-2.517938	-0.620763	-1.171017
O	-2.361230	-0.574011	1.432594
H	-5.285593	-0.629178	-0.407123
C	0.107705	0.694635	-0.038355
H	-3.959836	-1.313247	-0.812138
C	1.125548	1.669287	-0.132269
C	2.455264	1.305279	-0.123604
C	2.789444	-0.055679	-0.023531
C	1.793910	-1.042175	0.062804
C	0.457442	-0.675058	0.053041
H	0.834963	2.712545	-0.203633
H	3.234798	2.054158	-0.189667
N	4.171726	-0.434516	-0.010277
H	2.073824	-2.086291	0.137159
H	-0.317476	-1.425361	0.125372
O	4.467969	-1.639713	0.083983
O	5.039951	0.454140	-0.093588

PCM/B3LYP/6-31+G* Structure Obtained from Following the Intrinsic Reaction Coordinate (IRC) on the Optimized Transition State in the Product Direction for 50 Steps

O	3.672403	1.292039	-0.143707
P	3.039386	-0.092501	-0.133424
O	4.397652	-1.111967	0.107901
O	1.085767	1.185588	0.030327
O	2.351831	-0.535488	1.330243
O	2.380607	-0.728843	-1.344841
H	5.150116	-0.559861	0.376863
C	-0.106523	0.759403	0.012900
H	2.959924	-1.179667	1.732311
C	-1.178644	1.722814	0.036325
C	-2.490705	1.344361	0.032988
C	-2.824362	-0.033431	0.000404
C	-1.800551	-1.017154	-0.031149
C	-0.479564	-0.642237	-0.027230
H	-0.900561	2.773160	0.060640
H	-3.283802	2.082377	0.054232
N	-4.169327	-0.403652	-0.002675
H	-2.077496	-2.065386	-0.059699
H	0.309621	-1.380757	-0.063892
O	-4.487836	-1.623864	-0.036703
O	-5.060575	0.490121	0.028555

PCM/B3LYP/6-31+G* Reactant Complex Obtained from Following the Intrinsic Reaction Coordinate (IRC) in the Reactant Direction for 50 Steps, Followed by a Subsequent Geometry Optimzation

O	3.590293	-1.605749	-0.083691
P	2.595526	-0.509523	0.299295
O	4.666949	2.537542	-0.846061
O	1.092522	-1.288529	-0.235553
O	2.651055	0.768286	-0.561545
O	2.390745	-0.276201	1.798517
H	5.458662	2.034499	-1.092774
C	-0.139961	-0.787017	-0.145299
H	3.950369	1.854118	-0.711683
C	-1.200152	-1.614232	-0.593545
C	-2.510992	-1.176612	-0.546159
C	-2.789665	0.106631	-0.044097
C	-1.754785	0.941397	0.406888
C	-0.441784	0.501122	0.358704
H	-0.962841	-2.601620	-0.977239
H	-3.317525	-1.812736	-0.890375
N	-4.147871	0.568892	0.006840
H	-1.985412	1.928263	0.790216
H	0.359702	1.140333	0.703784
O	-4.382976	1.706566	0.454354
O	-5.055677	-0.180663	-0.398293

RELEVANT STATIONARY POINTS FOR *P*-NITROPHENYL SULFATE HYDROLYSIS

PCM/B3LYP/6-31+G* Optimized Geometry for p-Nitrophenyl Sulfate

S	-2.970280	-0.179354	0.002361
O	-4.083853	0.787130	-0.009429
O	-1.646022	0.939696	-0.010698
O	-2.802759	-0.941341	1.258310
O	-2.803666	-0.971995	-1.234607
C	-0.336717	0.558026	-0.005764
C	0.586481	1.621627	-0.001971
C	1.947784	1.364174	0.000622
C	2.388731	0.033437	-0.000303
C	0.115862	-0.772911	-0.005820
C	1.481448	-1.031251	-0.003374
H	-0.582279	-1.598869	-0.008903
H	1.840597	-2.053066	-0.004142
N	3.809524	-0.244441	0.001488
H	2.662008	2.178303	0.003707
H	0.216488	2.641482	-0.001214
O	4.186378	-1.425986	0.002531
O	4.602353	0.709283	0.001643

PCM/B3LYP/6-31+G* Optimized Approximate Transition State Geometry for p-Nitrophenyl Sulfate Hydrolysis (Structure Obtained from the Surface, Using S-O Constraints to the Nucleophile and Leaving Group)

O	-3.678557	1.272245	-0.027949
S	-2.991132	-0.014567	0.001302
O	-4.867176	-1.163605	0.010623
O	-0.884742	1.331898	-0.008577
O	-2.611264	-0.662485	-1.249569
O	-2.625420	-0.612223	1.281025
H	-5.441065	-0.930650	0.763835
C	0.315762	0.881676	-0.005983
H	-5.404221	-0.992268	-0.785073
C	1.440799	1.786789	-0.001689
C	2.738759	1.332627	0.001423
C	3.001951	-0.058731	0.000222
C	1.926849	-0.978854	-0.004227
C	0.626790	-0.527238	-0.006948
H	1.232727	2.853501	-0.002304
H	3.567368	2.031752	0.004386
N	4.331416	-0.526225	0.002564
H	2.137946	-2.042301	-0.005482
H	-0.192666	-1.237616	-0.011325
O	4.554722	-1.762906	-0.000929
O	5.279019	0.299152	0.007926

PCM/B3LYP/6-31+G* Optimized Reactant Complex (Obtained from Performing an Unconstrained Geometry Optimization on a Low-Energy Point in the Reactant Region of the Surface Shown in Fig. 5 of the Main Text)

S	-2.541895	-0.544208	0.447618
O	-3.614839	-1.268814	-0.253342
O	-1.223060	-0.928666	-0.593047
O	-2.642069	0.936774	0.393119
O	-2.153649	-1.078198	1.767789
C	0.066759	-0.544654	-0.352551
C	1.019549	-1.129409	-1.206793
C	2.362744	-0.815153	-1.074657
C	2.751271	0.089519	-0.076817
C	0.465521	0.363640	0.641878
C	1.812839	0.678121	0.777188
H	-0.259134	0.825397	1.298992
H	2.133289	1.376727	1.540152
N	4.153643	0.421074	0.075526
H	3.101460	-1.263392	-1.727350
H	0.687637	-1.828903	-1.966719
O	-4.371272	2.574931	-1.158053

H	-3.797789	1.941973	-0.675620
H	-4.778331	2.058277	-1.871369
O	4.485205	1.207708	0.974380
O	4.974133	-0.094065	-0.698115