Supplementary Material for Faraday Discussions

Ultrafast time-resolved transient infrared and resonance Raman spectroscopic study of the photo-deprotection and rearrangement reactions of *p*-hydroxyphenacyl caged phosphates

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Cartesian Coordinates for Reactions of HPDP (B3LYP/6-31G*)

HPDP-0W-RC

C	3.666913	-0.935020	0.871167
C	4.697654	-0.239484	0.272744
C	4.447382	0.547655	-0.864654
C	3.140340	0.634273	-1.382005
C	2.094465	-0.037847	-0.776859
C	2.334710	-0.879719	0.350989
O	5.503898	1.201597	-1.424775
C	1.292033	-1.628233	0.986727
O	1.506014	-1.997480	2.236630
C	-0.089258	-1.819120	0.454845
O	-1.001204	-0.756036	0.910847
P	-1.887690	0.049909	-0.155410
O	-1.227721	0.325716	-1.458587
O	-2.363745	1.332881	0.683442
C	-1.435137	2.429569	0.885949
C	-2.191460	3.560688	1.555557
O	-3.234823	-0.818963	-0.222294
C	-4.259676	-0.464495	-1.187043

C	-5.278483	-1.587589	-1.215862
H	5.712951	-0.303269	0.651484
H	3.864501	-1.567533	1.729700
H	2.946697	1.250860	-2.258555
H	1.088547	0.082693	-1.168601
H	-0.515637	-2.753536	0.827220
H	-0.062867	-1.833016	-0.637481
H	-0.611460	2.073002	1.514490
H	-1.030277	2.732145	-0.085401
H	-2.601384	3.236648	2.517123
H	-3.017015	3.902606	0.923257
H	-1.516677	4.405611	1.732427
H	-3.789176	-0.318974	-2.164835
H	-4.716493	0.480647	-0.872514
H	-4.810438	-2.526889	-1.526815
H	-5.723679	-1.732645	-0.226615
H	-6.078237	-1.346635	-1.925060
H	5.199754	1.683863	-2.210102

Sum of electronic and zero-point Energies= -1259.894463 a.u.

HPDP-0W-TS

C	2.483815	-0.898176	0.265404
C	3.858273	-0.969941	0.600546
C	4.767458	-0.093924	0.040370
C	4.312579	0.894369	-0.851384
C	2.943427	0.991661	-1.170913
C	2.030366	0.117418	-0.607083
O	5.239446	1.723937	-1.379713
C	1.539883	-1.850609	0.891587
C	0.321634	-2.251232	0.325268
O	1.914802	-2.295075	2.033353
O	-1.125953	-0.767980	1.185075
P	-1.876927	-0.035609	0.055236
O	-3.172503	-0.937134	-0.294421
C	-4.043458	-0.535712	-1.371705
C	-5.065769	-1.637898	-1.584256
O	-1.069482	0.328401	-1.165082
O	-2.611173	1.265013	0.707911
C	-1.804543	2.403135	1.063749
C	-2.730689	3.512428	1.529564
H	5.827448	-0.152060	0.263692
H	4.191122	-1.738213	1.289212
H	2.602074	1.756928	-1.865459
H	0.970544	0.213442	-0.841760

H	-0.273106	-2.995439	0.835602
H	0.112506	-2.031045	-0.714094
H	-1.109553	2.109668	1.860296
H	-1.218123	2.712648	0.190462
H	-3.317882	3.186988	2.394125
H	-3.422544	3.798847	0.730796
H	-2.147925	4.394966	1.817563
H	-3.443881	-0.366447	-2.273189
H	-4.532174	0.407488	-1.099484
H	-4.571687	-2.577125	-1.853458
H	-5.648953	-1.804788	-0.673028
H	-5.753513	-1.362901	-2.392197
H	4.810591	2.354757	-1.981490

Sum of electronic and zero-point Energies= -1259.877645 a.u.

HPDP-0W-PR

C	-4.674278	-0.501555	-0.054285
C	-5.152824	0.717168	0.399619
C	-4.246793	1.740934	0.712368
C	-2.870948	1.527861	0.564118
C	-2.400296	0.299652	0.108166
C	-3.295247	-0.736652	-0.206118
O	-4.764318	2.922088	1.155218
C	-2.867459	-2.083444	-0.702046
O	-3.724764	-2.936556	-1.007548
C	-1.472621	-2.411236	-0.825137
O	2.544930	-1.524154	-1.391738
P	2.539152	-0.444976	-0.299046
O	1.068558	-0.106812	-0.081168
O	3.411902	0.842945	-0.685691
C	3.014611	1.660972	-1.824713
C	4.033099	2.772478	-1.978083
O	3.313898	-0.990321	0.976783
C	3.740728	-0.134515	2.073068
C	4.402133	-1.016640	3.112971
H	-6.215572	0.901663	0.521116
H	-5.357427	-1.307001	-0.302298
H	-2.168830	2.324289	0.805551
H	-1.329067	0.166788	-0.000339
H	-1.229065	-3.401131	-1.195009
H	-0.663757	-1.737301	-0.567407
H	2.979807	1.018842	-2.710622
H	2.009590	2.050127	-1.634289
H	5.031871	2.362691	-2.156867

H	4.067515	3.397007	-1.079783
H	3.761074	3.405962	-2.829360
H	2.861061	0.373929	2.482541
H	4.430678	0.615467	1.676124
H	3.699993	-1.766271	3.489854
H	5.267966	-1.533172	2.687695
H	4.741755	-0.402827	3.954562
H	-4.037143	3.537923	1.337803

Sum of electronic and zero-point Energies=-1259.888372 a.u.

HPDP-2W-RC

C	-3.819633	-0.827904	-1.176453
C	-4.935171	-0.347205	-0.519296
C	-4.797183	0.299331	0.720258
C	-3.518365	0.464565	1.283114
C	-2.392261	0.006160	0.621707
C	-2.513104	-0.688005	-0.616202
O	-5.933275	0.743013	1.330661
C	-1.372200	-1.203890	-1.314812
O	-1.514270	-1.405225	-2.613994
C	0.005406	-1.310209	-0.766744
O	0.749040	-0.024223	-0.965088
P	1.662766	0.575128	0.195495
O	1.027887	0.703403	1.541290
O	2.190049	1.940802	-0.448368
C	1.273417	3.058792	-0.605319
C	2.074870	4.246138	-1.101733
O	2.988027	-0.336731	0.163830
C	3.712304	-0.665833	1.394718
C	4.982914	-1.385994	0.987659
O	0.723257	-1.858301	2.565563
O	2.882087	-2.567116	-1.775966
H	-5.930124	-0.475763	-0.933879
H	-3.930115	-1.353601	-2.118860
H	-3.411288	0.974901	2.239240
H	-1.412922	0.184130	1.053666
H	0.598099	-2.059028	-1.295688
H	-0.026572	-1.551227	0.299876
H	0.497217	2.769746	-1.321829
H	0.803448	3.264598	0.362003
H	2.551496	4.018467	-2.060151
H	2.852922	4.517447	-0.381484
H	1.412660	5.108056	-1.239402
H	3.062892	-1.292750	2.010658

H	3.927386	0.263081	1.931263
H	4.751502	-2.277322	0.395605
H	5.632261	-0.733152	0.395503
H	5.529389	-1.698506	1.884273
H	-5.700570	1.150090	2.180130
H	0.023763	-2.009385	3.217893
H	0.744078	-0.888362	2.429602
H	3.001615	-2.159150	-2.646865
H	2.973005	-1.819834	-1.158789

Sum of electronic and zero-point Energies= -1412.691669 a.u.

HPDP-2W-TS

C	-4.970998	-0.236800	-0.238696
C	-4.644645	0.845597	0.598396
C	-3.296046	1.155824	0.873906
C	-2.279025	0.404886	0.314348
C	-2.599755	-0.713933	-0.492075
C	-3.958369	-0.997188	-0.788518
O	-5.669693	1.557312	1.114877
C	-1.537482	-1.539077	-1.096423
C	-0.285220	-1.806564	-0.516773
O	-1.850709	-1.868128	-2.306550
O	0.889109	-0.289911	-1.146905
P	1.667676	0.409071	-0.002651
O	2.636707	1.517690	-0.680680
C	2.076555	2.786643	-1.081854
C	3.215173	3.670021	-1.558128
O	2.756909	-0.685766	0.488341
C	3.430445	-0.509855	1.760610
C	4.496737	-1.583196	1.873622
O	0.865698	0.987240	1.136631
O	0.115756	-1.117718	2.731014
H	-6.016075	-0.457503	-0.427822
H	-4.192305	-1.839793	-1.429331
H	-3.055828	1.997674	1.520506
H	-1.240501	0.661830	0.509673
H	0.383634	-2.509156	-1.002537
H	-0.204768	-1.680894	0.560864
H	1.349505	2.615336	-1.885112
H	1.553238	3.231384	-0.228024
H	3.735621	3.207504	-2.402583
H	3.939552	3.834072	-0.753814
H	2.826577	4.643061	-1.879617
H	2.688214	-0.598733	2.558960

H	3.874758	0.491370	1.794862
H	4.046566	-2.580366	1.828420
H	5.229971	-1.493522	1.065464
H	5.022231	-1.487784	2.830571
H	-5.326788	2.272088	1.676522
H	-0.507143	-0.874211	3.431028
H	0.360623	-0.266086	2.300172
H	2.043991	-1.749329	-2.126707
O	2.468732	-2.602401	-1.926365
H	2.889506	-2.397705	-1.075127

Sum of electronic and zero-point Energies= -1412.683804 a.u.

HPDP-2W-PR

C	-3.971985	-1.007615	-0.738461
C	-4.969599	-0.211910	-0.213108
C	-4.619835	0.904413	0.569561
C	-3.264290	1.211294	0.816996
C	-2.262211	0.422484	0.284270
C	-2.608004	-0.728111	-0.465085
O	-5.629413	1.651253	1.061809
C	-1.559275	-1.593956	-1.045584
O	-1.881096	-1.939264	-2.242232
C	-0.329862	-1.890222	-0.443473
O	0.894575	-0.305247	-1.171261
P	1.664512	0.400664	-0.033889
O	0.857739	1.011245	1.087844
O	2.665470	1.490394	-0.702942
C	2.134868	2.767070	-1.114123
C	3.295067	3.626567	-1.582763
O	2.734900	-0.697186	0.496690
C	3.410005	-0.487629	1.761257
C	4.472474	-1.561485	1.904944
O	0.083684	-1.033405	2.739786
O	2.408047	-2.664116	-1.874962
H	-6.019354	-0.427135	-0.381076
H	-4.221347	-1.874019	-1.340514
H	-3.007674	2.079044	1.421589
H	-1.218441	0.675155	0.459625
H	0.358382	-2.575137	-0.927688
H	-0.237498	-1.712503	0.625638
H	1.412216	2.608508	-1.924284
H	1.611778	3.226258	-0.267645
H	3.813983	3.151152	-2.421016
H	4.015375	3.778100	-0.772297

H	2.929450	4.606499	-1.910443
H	2.668778	-0.550130	2.563310
H	3.859064	0.512154	1.767154
H	4.018579	-2.557913	1.887822
H	5.205252	-1.497506	1.093932
H	4.999210	-1.441386	2.858483
H	-5.273343	2.388565	1.585210
H	-0.504524	-0.746066	3.452934
H	0.348176	-0.203472	2.277212
H	1.989849	-1.805392	-2.070008
H	2.849053	-2.459532	-1.034049

Sum of electronic and zero-point Energies= -1412.683696 a.u.

HPDP-4W-RC

C	2.618012	2.982253	-0.017593
C	3.853634	2.470417	0.241054
C	4.070827	1.052787	0.260038
C	2.959036	0.170874	0.041461
C	1.714367	0.671447	-0.205640
C	1.487766	2.106654	-0.308304
O	5.302681	0.613102	0.503694
C	0.238753	2.686338	-0.669089
C	-0.908784	1.818758	-1.097162
O	-1.574507	1.203239	0.094066
P	-2.225201	-0.238336	0.033842
O	-1.319400	-1.417861	-0.134346
O	0.074219	3.962268	-0.621427
O	-3.308615	-0.095346	-1.148323
C	-3.927597	-1.278893	-1.721163
C	-4.745920	-0.839989	-2.919973
O	-3.012664	-0.354549	1.419756
C	-3.843265	0.732338	1.920238
C	-4.483621	0.263588	3.211793
O	5.492982	-2.010054	0.488782
O	3.798596	-3.263482	-1.176147
O	1.217116	-2.912629	-0.448233
O	-0.137709	-2.906284	1.933282
H	2.433080	4.048904	-0.046212
H	4.707317	3.113876	0.433130
H	3.113092	-0.901906	0.080306
H	0.884285	-0.015681	-0.313746
H	5.353621	-0.397427	0.489739
H	-0.604109	1.003425	-1.761732
H	-1.665673	2.435068	-1.582555

H	5.330783	-2.412914	1.354566
H	4.895130	-2.498901	-0.144501
H	2.841715	-3.159288	-0.932716
H	3.865389	-2.915464	-2.077390
H	0.500335	-2.367841	-0.813401
H	0.931740	-3.037441	0.488018
H	-0.677886	-3.710278	1.973186
H	-0.689436	-2.277322	1.419055
H	-3.140674	-1.985477	-2.000872
H	-4.559309	-1.747206	-0.957246
H	-3.206006	1.607010	2.074798
H	-4.595654	0.975827	1.162018
H	-5.233919	-1.709410	-3.374080
H	-5.518855	-0.124090	-2.623689
H	-4.107135	-0.368162	-3.672964
H	-5.109635	1.062622	3.623936
H	-5.112178	-0.616102	3.040923
H	-3.718863	0.006564	3.951015

Sum of electronic and zero-point Energies= -1565.523670 a.u.

HPDP-4W-TS

C	-4.008570	2.382939	-0.071123
C	-4.120976	0.967909	-0.149138
C	-2.943816	0.167003	-0.088785
C	-1.711106	0.762068	0.044094
C	-1.594661	2.173816	0.200805
C	-2.777399	2.970086	0.085053
O	-5.332337	0.449881	-0.279628
C	-0.309485	2.828372	0.411536
O	-0.232415	4.019463	-0.100981
C	0.834458	2.166293	0.965460
O	1.740006	1.329193	-0.268257
P	2.219197	-0.132047	-0.039625
O	3.059157	-0.058234	1.345534
C	3.510788	-1.283309	1.969761
C	4.189681	-0.920236	3.277305
O	3.283556	-0.452165	-1.207635
C	4.274122	0.534911	-1.591706
C	5.158186	-0.086739	-2.656257
O	1.208666	-1.246704	-0.014936
O	-5.395571	-2.158821	-0.392616
O	-3.611441	-3.589875	0.989931
O	-1.220964	-2.743869	0.097355
O	0.223757	-2.634485	-2.217760

H	-2.677855	4.046720	0.158199
H	-4.919124	2.971543	-0.120725
H	-3.015697	-0.913235	-0.154278
H	-0.821328	0.142563	0.037010
H	-5.318302	-0.564642	-0.310660
H	0.615920	1.365459	1.666559
H	1.629744	2.829750	1.287893
H	-5.317986	-2.506436	-1.293301
H	-4.757760	-2.702213	0.155085
H	-2.694022	-3.341679	0.700745
H	-3.635502	-3.401652	1.939521
H	-0.477668	-2.251973	0.489981
H	-0.912343	-2.869142	-0.831786
H	0.812898	-3.401261	-2.284736
H	0.716072	-2.013043	-1.634357
H	2.648409	-1.938393	2.129986
H	4.205831	-1.792746	1.291123
H	3.754987	1.422945	-1.963411
H	4.855524	0.819154	-0.706661
H	4.545016	-1.827264	3.778923
H	5.047114	-0.262861	3.101617
H	3.492088	-0.405526	3.945719
H	5.916890	0.635114	-2.978605
H	5.667510	-0.975949	-2.270909
H	4.564979	-0.378278	-3.528621

Sum of electronic and zero-point Energies= -1565.521559 a.u.

HPDP-4W-PR

C	-2.976174	2.938964	-0.033096
C	-4.117077	2.184237	-0.093392
C	-4.020654	0.758151	-0.158736
C	-2.734783	0.128389	-0.186196
C	-1.598318	0.899423	-0.125157
C	-1.695877	2.310290	0.016589
O	-5.137978	0.081224	-0.194848
C	-0.484763	3.169060	0.116734
C	0.665626	2.779075	0.827539
O	1.782652	1.326076	-0.638157
P	2.149878	-0.046499	-0.117875
O	1.112378	-1.156478	-0.082740
O	-0.579996	4.251943	-0.530514
O	2.748715	0.181170	1.391991
C	3.121493	-0.966149	2.175071
C	3.606272	-0.478884	3.529812

O	3.405456	-0.656337	-0.962478
C	4.460380	0.233106	-1.380209
C	5.476173	-0.579860	-2.163347
O	-4.980825	-2.450283	-0.286833
O	-3.260867	-3.859109	1.128210
O	-1.184028	-2.653524	0.011331
O	0.406129	-2.774178	-2.177860
H	-3.019601	4.021403	0.010413
H	-5.106794	2.628447	-0.084475
H	-2.645891	-0.953684	-0.248352
H	-0.622655	0.425177	-0.178340
H	-5.010044	-0.950739	-0.226843
H	0.639532	1.963483	1.537154
H	1.532981	3.424899	0.813553
H	-4.842024	-2.807912	-1.176567
H	-4.363731	-2.978331	0.312882
H	-2.387674	-3.511276	0.792851
H	-3.258430	-3.689922	2.081761
H	-0.437456	-2.122170	0.361333
H	-0.813898	-2.926595	-0.865089
H	1.059848	-3.489045	-2.143511
H	0.810554	-2.067487	-1.615340
H	2.256257	-1.631471	2.276794
H	3.911638	-1.520311	1.652438
H	4.031267	1.035322	-1.988750
H	4.922048	0.689648	-0.494979
H	3.901373	-1.328910	4.155760
H	4.469827	0.184717	3.417109
H	2.815562	0.074177	4.047926
H	6.295084	0.064677	-2.503033
H	5.898288	-1.378025	-1.543552
H	5.008897	-1.037434	-3.041485

Sum of electronic and zero-point Energies= -1565.527295 a.u.