Supporting Information

A Computational Study of the Phosphoryl Donor Activity of Dihydroxyacetone Kinase from ATP to Inorganic Polyphoshate

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Table S1. Cartesian coordinates of the QM atoms of the TS localized at B3LYP/MM level of the *substrate-assisted mechanism* in the wild type enzyme.

DHA			
$C1_{Dha}$	-0.20448	-2.72954	4.37691
$C2_{Dha}$	1.29355	-2.41636	4.71958
$H21_{Dha}$	1.73460	-3.40182	4.94774
$H22_{Dha}$	1.29002	-1.83492	5.65412
$C3_{Dha}$	-0.37011	-3.61573	3.12463
$H31_{Dha}$	0.37247	-3.28667	2.38420
$H32_{Dha}$	-1.37146	-3.43140	2.69184
$O4_{Dha}$	-0.82532	-3.27713	5.48822
$O5_{Dha}$	1.94271	-1.76005	3.67296
$H5_{Dha}$	3.43642	-2.09664	3.24831
$O6_{Dha}$	-0.20929	-4.95286	3.51750
$H6_{Dha}$	0.03977	-5.50278	2.73454
POLY-P			
$O1_{poly\text{-}P}$	3.61869	0.12918	5.18274
$P2_{poly\text{-}P}$	3.51287	-0.18740	3.72877
$O3_{poly\text{-}P}$	6.11671	0.68159	3.68089
$O4_{poly\text{-}P}$	2.95403	0.73864	2.69810
$O5_{poly\text{-}P}$	4.25555	-1.50622	3.17463
$P6_{poly\text{-}P}$	7.65303	1.12838	3.57446
$O7_{poly\text{-}P}$	8.10670	1.12029	5.21934
$O8_{poly\text{-}P}$	8.48678	0.09530	2.82397
$O9_{poly\text{-}P}$	7.76466	2.58343	3.09799
$P10_{poly\text{-}P}$	9.40877	0.80886	6.34731
$O11_{poly\text{-}P}$	10.73144	1.56735	5.87856
$O12_{poly\text{-}P}$	8.76991	1.50971	7.57795
$O13_{poly\text{-}P}$	9.43241	-0.70593	6.49587
HIS 61			
CB_{His61}	-6.85799	-5.94647	4.92303
$HB1_{His61}$	-7.16370	-6.34866	3.94874
$HB2_{His61}$	-6.61650	-6.81175	5.54947

CG_{His61}	-5.61413	-5.12750	4.73339
$ND1_{His61}$	-5.30952	-4.54078	3.51604
$HD1_{His61}$	-5.94904	-4.47590	2.73808
$CE1_{His61}$	-4.09172	-3.93602	3.62251
$HE1_{His61}$	-3.62923	-3.38770	2.81462
$NE2_{His61}$	-3.57945	-4.11195	4.82482
$HE2_{His61}$	-1.69588	-3.67120	5.23294
$CD2_{His61}$	-4.52545	-4.84082	5.52268
$HD2_{His61}$	-4.38516	-5.10562	6.55862
HIS 220			
CB_{His220}	-2.26624	1.69292	5.56779
$HB1_{His220}$	-1.70597	1.69990	6.50840
$HB2_{His220}$	-1.94790	2.60150	5.06155
CG_{His220}	-1.76432	0.53893	4.75531
$ND1_{His220}$	-0.91820	0.73319	3.66932
$HD1_{His220}$	-0.56531	1.68672	3.28262
$CE1_{His220}$	-0.36410	-0.42687	3.31304
$HE1_{His220}$	0.42208	-0.55514	2.59194
$NE2_{His220}$	-0.84785	-1.38251	4.11648
$CD2_{His220}$	-1.73542	-0.79993	5.00792
$HD2_{His220}$	-2.21722	-1.38725	5.76635
ASP 114			
CB_{Asp114}	1.94051	-5.25047	0.34956
$HB1_{Asp114}$	2.00473	-4.67152	-0.57525
$HB2_{Asp114}$	1.74609	-4.56514	1.18219
CG_{Asp114}	0.72403	-6.19468	0.26521
$OD1_{Asp114}$	0.19182	-6.53922	1.38772
$OD2_{Asp114}$	0.25732	-6.54246	-0.84406

Table S2. Cartesian coordinates of the QM atoms of the TS localized at B3LYP/MM level of the *substrate-assisted mechanism* in the mutated enzyme.

DHA			
$C1_{Dha}$	-0.07479	-2.68209	4.35110
$C2_{Dha}$	1.43005	-2.36600	4.65771
$H21_{Dha}$	1.88634	-3.34884	4.87109
$H22_{Dha}$	1.45653	-1.78329	5.59081
$C3_{Dha}$	-0.27010	-3.54421	3.08430
$H31_{Dha}$	0.49316	-3.23387	2.35701
$H32_{Dha}$	-1.25929	-3.30664	2.64746
$O4_{Dha}$	-0.67308	-3.25984	5.46299
$O5_{Dha}$	2.037549	-1.70614	3.58874
$H5_{Dha}$	3.576659	-2.07227	3.15810
$O6_{Dha}$	-0.17640	-4.89796	3.45609
$H6_{Dha}$	0.13280	-5.44049	2.69264
POLY-P			
$O1_{poly\text{-}P}$	3.62199	0.15711	5.11157
$P2_{poly\text{-}P}$	3.56018	-0.15890	3.65448
$O3_{poly\text{-}P}$	6.11890	0.68195	3.62338
$O4_{poly\text{-}P}$	3.00340	0.75502	2.60928

$O5_{poly\text{-}P}$	4.35993	-1.45489	3.11082
$P6_{poly\text{-}P}$	7.66808	1.10794	3.53945
$O7_{poly\text{-}P}$	8.11086	1.03413	5.18477
$O8_{poly\text{-}P}$	8.48587	0.06899	2.78009
$O9_{poly\text{-}P}$	7.80111	2.56535	3.09366
$P10_{poly\text{-}P}$	9.41942	0.82030	6.32814
$O11_{poly\text{-}P}$	10.72814	1.54975	5.81216
$O12_{poly\text{-}P}$	8.76292	1.54968	7.52738
$O13_{poly\text{-}P}$	9.49269	-0.68770	6.55775
HIS 61			
CB_{His61}	-6.82020	-5.93556	4.89874
$HB1_{His61}$	-7.13749	-6.33548	3.92649
$HB2_{His61}$	-6.56810	-6.80365	5.51732
CG_{His61}	-5.57272	-5.12328	4.68807
$ND1_{His61}$	-5.27160	-4.55384	3.45983
$HD1_{His61}$	-5.92199	-4.47492	2.69166
$CE1_{His61}$	-4.03939	-3.97087	3.54663
$HE1_{His61}$	-3.58045	-3.43365	2.72779
$NE2_{His61}$	-3.51388	-4.14704	4.74326
$HE2_{His61}$	-1.52921	-3.67010	5.19915
$CD2_{His61}$	-4.46658	-4.85067	5.45881
$HD2_{His61}$	-4.31802	-5.11001	6.49538
HIS 220			
CB_{His220}	-2.18375	1.70823	5.57561
$HB1_{His220}$	-1.63312	1.73152	6.52153
$HB2_{His220}$	-1.88324	2.62118	5.06680
CG_{His220}	-1.66352	0.55989	4.77657
$ND1_{His220}$	-0.85286	0.76187	3.66998
$HD1_{His220}$	-0.52739	1.72979	3.26898
$CE1_{His220}$	-0.28172	-0.38585	3.30839
$HE1_{His220}$	0.49497	-0.49983	2.57566
$NE2_{His220}$	-0.72701	-1.34392	4.13053
$CD2_{His220}$	-1.60134	-0.77491	5.04244
$HD2_{His220}$	-2.04737	-1.36244	5.82257
ASP 114			
CB_{Asp114}	2.01819	-5.16902	0.38555
$HB1_{Asp114}$	2.10672	-4.58027	-0.53140
$HB2_{Asp114}$	1.81639	-4.48924	1.21999
CG_{Asp114}	0.80899	-6.11491	0.27608
$OD1_{Asp114}$	0.31789	-6.52974	1.39364
$OD2_{Asp114}$	0.31482	-6.41197	-0.83673

Table S3. Atomic charges on key atoms of the TS localized at B3LYP/MM level of the *substrate-assisted mechanism* in the wild type enzyme.

$O5_{Dha}$	-0.662
$H5_{Dha}$	0.344
$O1_{poly\text{-}P}$	-0.739
$P2_{poly\text{-}P}$	1.107
$O3_{poly\text{-}P}$	-1.044
$O4_{poly\text{-}P}$	-0.651
$O5_{poly\text{-}P}$	-0.616
$P6_{poly\text{-}P}$	1.368
$O7_{poly\text{-}P}$	-0.885
$O8_{poly\text{-}P}$	-0.910

Table S4. Atomic charges on key atoms of the TS localized at B3LYP/MM level of the *substrate-assisted mechanism* in the mutated enzyme.

$O5_{Dha}$	-0.615
$H5_{Dha}$	0.342
$O1_{poly\text{-}P}$	-0.738
$P2_{poly\text{-}P}$	1.102
$O3_{poly\text{-}P}$	-1.049
$O4_{poly\text{-}P}$	-0.656
$O5_{poly\text{-}P}$	-0.618
$P6_{poly\text{-}P}$	1.383
$O7_{poly\text{-}P}$	-0.874
$O8_{poly\text{-}P}$	-0.890