Electronic Supplementary Material for PCCP

Alkali Metals (Li, Na, and K) in Methyl Phosphodiester Hydrolysis

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Electronic Supplementary Information:

Table 1S. ρ_{bcp} for bond formed (or cleaved) in SP along the hydrolysis pathways catalyzed by different alkali metals.

	Electron density (ρ_{bcp}) at O_3P_2 bond				Electron density (ρ_{bcp}) at O_1P_2 bond			
	D-Li	E-Li	E-Na	E-K	D-Li	E-Li	E-Na	E-K
R					0.147	0.143	0.145	0.146
TS1	0.043	0.041	0.045	0.050	0.126	0.129	0.126	0.124
I1	0.094	0.098	0.097	0.098	0.112	0.113	0.111	0.110
TS2	0.104	0.107	0.106	0.102	0.094	0.092	0.092	0.103
I2	0.111	0.113	0.115	0.105	0.087	0.089	0.074	0.103
TS3	0.122	0.125	0.118	0.121	0.047	0.045	0.064	0.054
P	0.143	0.139	0.146	0.147				

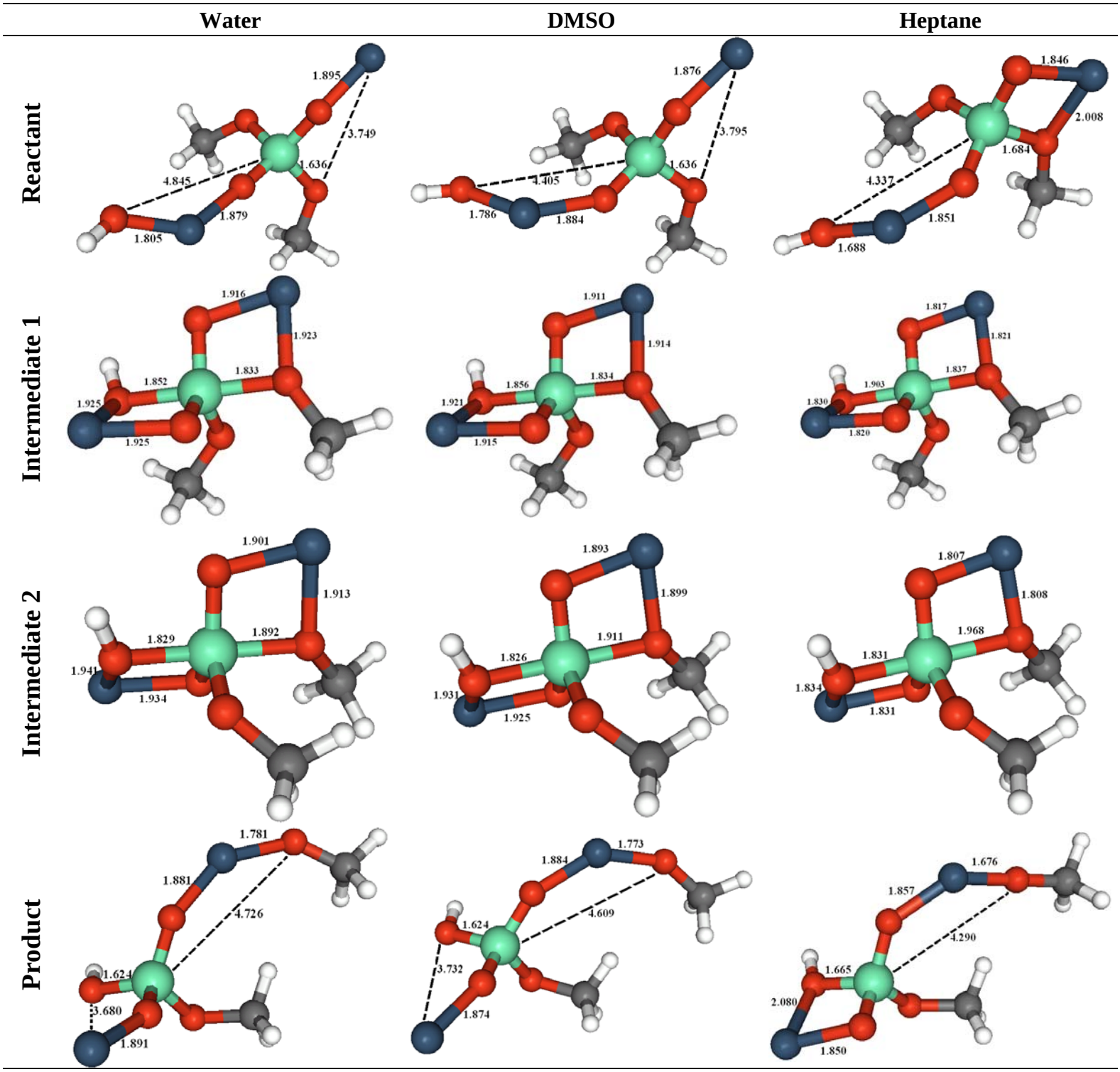

Figure 1S. Optimized structures for the minima along the 'E' profile for the lithium catalyzed MPDE hydrolysis in different solvents.

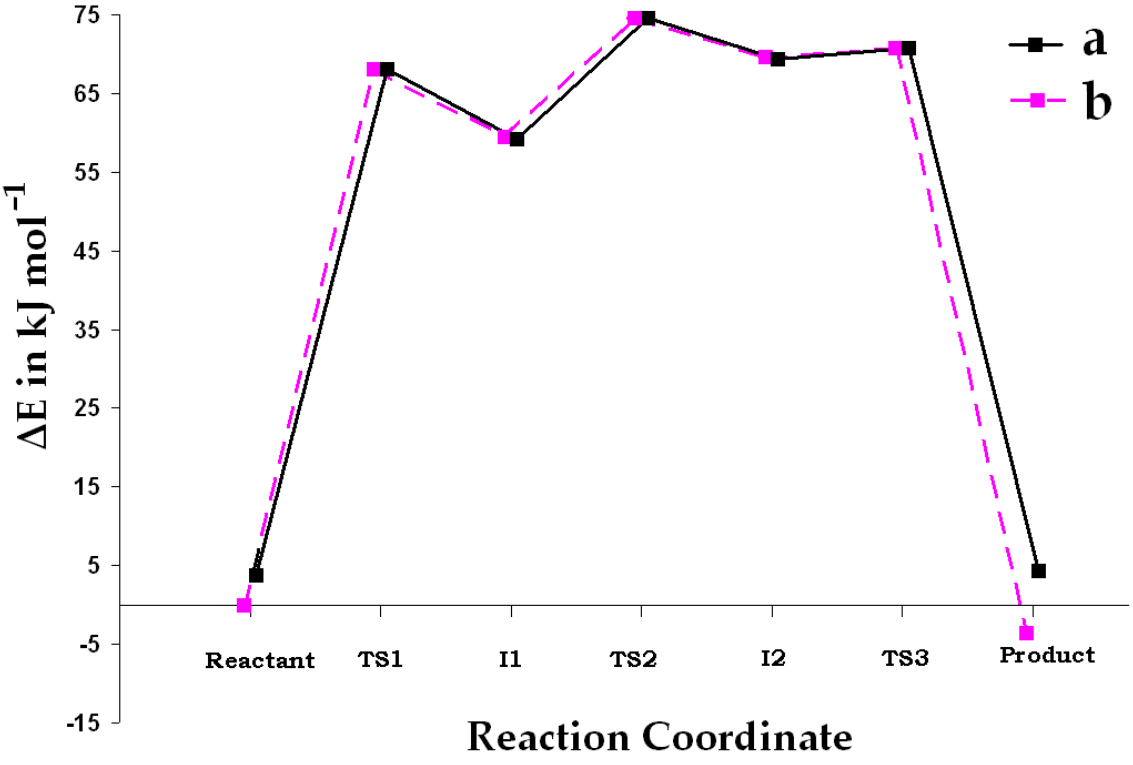

Figure 2S. Relative energies (in kJ mol^{-1}) of SP geometries in Li catalyzed mechanism 'E' in water. (a) Energetics for stationary point geometries viz. reactant, TS, intermediate and products obtained from scans along the reaction coordinates. (b) Energetics for the optimized geometries of the minima on the PES. The optimization of TS fails trough out in the solvents. Thus energies of TS considered hers are from the scan.

Table 3S: Atomic coordinates in the stationary point geometries on the PES of the metal catalyzed MPDE hydrolysis pathways calculated from the B3LYP/6-31+G(d,p) theory.

D-Li2-Reactant				E-Li2-Reactant			
C	-2.944249	0.304101	-0.467486	C	1.418202	2.086177	-0.261095
O	-1.796391	-0.572192	-0.467766	O	1.765881	0.694654	-0.136741
P	-0.397252	-0.107729	0.354195	P	0.571175	-0.520193	-0.118525
O	-0.660847	0.341611	1.743088	O	-0.059753	-0.439865	1.348213
O	0.113557	1.035035	-0.653362	C	-1.288481	0.265495	1.694472
C	1.228477	1.902627	-0.276271	O	1.524943	-1.704105	-0.173893
O	0.382405	-1.433718	0.076761	O	-0.413671	-0.221121	-1.215647
Li	-0.955453	-2.201624	-0.877720	Li	3.034392	-0.738317	-0.202709
Li	2.261094	-1.356567	0.124047	Li	-2.234464	-0.151480	-1.441285
O	3.592678	-0.446354	-0.230621	H	-2.095261	0.096099	0.969494
H	2.161929	1.324192	-0.271678	H	-1.078824	1.335836	1.783088
H	1.028837	2.349674	0.700983	H	-1.573385	-0.129121	2.670483
H	1.259151	2.676648	-1.043869	H	2.333923	2.631206	-0.498141
H	-3.772933	-0.252179	-0.908515	H	1.008557	2.457063	0.683010
H	-2.726519	1.191193	-1.067381	H	0.688745	2.217028	-1.064063
H	-3.185967	0.590620	0.558581	O	-3.624998	0.118745	-0.573454
H	4.520775	-0.225043	-0.302277	H	-4.568697	0.167684	-0.422113
D-Li2-TS1				E-Li2-TS1			
C	-2.600664	0.635633	0.235783	C	-2.481024	0.808667	0.498842
O	-1.718087	-0.376085	-0.246555	O	-1.772713	-0.248786	-0.144722
P	0.005051	-0.257881	0.164707	P	-0.019911	-0.346485	-0.001686
O	0.256264	-1.647136	-0.555166	O	0.229460	1.017869	-0.838766
O	-0.008961	-0.001258	1.635222	C	1.217549	2.003302	-0.489002
O	0.247541	0.986946	-0.848331	O	0.037111	-1.638031	-0.827576
C	1.089858	2.101828	-0.498822	O	0.165502	-0.227998	1.509913
Li	-1.451873	-1.968423	-1.017076	Li	-1.711778	-1.772815	-1.157117
Li	2.064137	-1.827984	-0.414566	O	2.384224	-0.558342	0.071164
O	2.381323	-0.326585	0.313273	Li	1.924577	-0.632638	1.720076
H	2.134117	1.789238	-0.518679	H	2.209346	1.549846	-0.509764
H	0.834143	2.476158	0.497195	H	1.008368	2.413385	0.505797
H	0.883401	2.869498	-1.248477	H	1.118756	2.794465	-1.235693
H	-2.485733	0.748149	1.317862	H	-3.551199	0.638157	0.349115
H	-3.624907	0.331191	0.000478	H	-2.204106	1.772904	0.058339
H	-2.386503	1.590238	-0.257811	H	-2.255558	0.815617	1.569714
H	2.533122	-0.058847	1.224432	H	2.566839	-1.200252	-0.620250
D-Li2-Intermidiate-1				E-Li2-Intermidiate-1			
C	-2.530217	0.646615	0.223479	P	0.094324	-0.377244	-0.008802
O	-1.664455	-0.355628	-0.281127	O	-0.019417	-1.613461	-0.944357
P	0.121357	-0.275112	0.181186	O	0.085253	-0.346101	1.540690
O	0.276128	-1.661994	-0.618930	O	0.291828	1.080744	-0.750037
O	-0.061858	-0.067134	1.662888	O	-1.719815	-0.143933	-0.190319
O	0.258654	1.025977	-0.820916	C	-2.373667	0.893268	0.517833
C	1.108329	2.130477	-0.496782	C	1.366670	1.973076	-0.460539
Li	-1.435474	-1.892038	-1.090427	H	1.477912	2.123797	0.620176
Li	2.042152	-1.890519	-0.432995	H	1.097859	2.925772	-0.925625
O	2.070475	-0.328540	0.362721	H	2.310779	1.606196	-0.868751
H	2.156521	1.884872	-0.682678	H	-3.453764	0.802763	0.351282
H	0.985826	2.427169	0.550682	H	-2.042342	1.875942	0.158095
H	0.791034	2.952647	-1.144119	H	-2.164391	0.814704	1.590449

H	-2.445668	0.708106	1.313507	Li	1.775884	-0.818296	1.831021
H	-3.559904	0.388975	-0.051481	Li	-1.765398	-1.560002	-1.267063
H	-2.283127	1.623177	-0.212558	O	2.007884	-0.639627	0.071021
H	2.214701	-0.074597	1.281861	H	2.203759	-1.254647	-0.645226
D-Li2-TS2 (-CH3 rotation)				E-Li2-TS2 (-CH3 rotation)			
C	-2.567117	-0.423455	0.428410	C	-2.510654	-0.086323	0.692341
O	-1.433231	-0.727600	-0.360697	O	-1.555078	-0.502344	-0.260241
P	0.360302	-0.155420	0.163451	Li	-1.173764	-1.868707	-1.315112
O	0.860302	-1.426400	-0.671699	O	0.531438	-1.557228	-0.920950
O	-0.003207	0.023507	1.614783	P	0.380990	-0.296288	-0.042470
O	0.270939	1.095836	-0.896014	O	0.342719	1.058503	-0.967841
C	-0.431806	2.280643	-0.521503	C	-0.156713	2.285089	-0.445540
Li	-0.717483	-2.026231	-1.274683	O	2.237664	-0.133599	0.167069
Li	2.631020	-1.204239	-0.433910	O	0.241302	-0.123729	1.489155
O	2.190857	0.231664	0.472057	Li	1.977949	-0.144428	1.920226
H	-0.124605	2.633046	0.468889	H	-1.228121	2.219328	-0.230755
H	-1.514112	2.112572	-0.523948	H	0.009638	3.039556	-1.218458
H	-0.182854	3.036199	-1.270697	H	0.376350	2.580810	0.465907
H	-2.269771	-0.245716	1.466458	H	-3.310126	-0.838043	0.780062
H	-3.278602	-1.261928	0.398089	H	-2.983281	0.863934	0.396526
H	-3.088140	0.468952	0.048832	H	-2.044829	0.042007	1.674903
H	2.221204	0.560403	1.377499	H	2.672811	-0.549285	-0.584820
D-Li2-Intermidiate-2				E-Li2-Intermidiate-2			
C	2.454378	-0.726294	0.482080	C	2.387684	-0.579797	0.733734
O	1.357596	-0.722628	-0.410861	O	1.444572	-0.591134	-0.318208
P	-0.447707	-0.095017	0.176604	Li	0.920508	-1.715610	-1.581806
O	-0.991358	-1.222638	-0.829403	O	-0.735672	-1.224256	-1.197848
O	-0.117609	-0.202234	1.640993	P	-0.479943	-0.195570	-0.068228
O	-0.207484	1.316275	-0.628047	O	-0.254600	1.341620	-0.596031
C	1.008735	2.054173	-0.500362	C	0.885375	2.131931	-0.269167
Li	0.553856	-1.887133	-1.428523	O	-2.278062	0.168075	0.109659
Li	-2.750631	-0.924373	-0.608347	O	-0.377179	-0.422717	1.459959
O	-2.215498	0.396110	0.419113	Li	-2.108762	-0.209712	1.847832
H	1.325150	2.118440	0.546112	H	1.773664	1.784622	-0.803338
H	1.805177	1.598985	-1.095136	H	0.641049	3.152094	-0.577133
H	0.791833	3.058578	-0.873280	H	1.082827	2.120994	0.808672
H	2.102642	-0.750226	1.518717	H	3.135330	-1.371852	0.575209
H	3.087690	-1.607460	0.297152	H	2.928815	0.378700	0.780494
H	3.083583	0.167358	0.346001	H	1.894875	-0.746887	1.697363
H	-2.273995	0.787743	1.297307	H	-2.723463	-0.093664	-0.703575
D-Li2-TS3				E-Li2-TS3			
C	-2.630197	-0.604427	0.488427	C	-2.596886	-0.421852	0.731917
O	-1.581665	-0.720793	-0.429239	O	-1.704752	-0.554980	-0.331393
P	0.563254	-0.069684	0.193665	Li	-1.056132	-1.698295	-1.432664
O	0.936691	-1.286402	-0.754630	O	0.676252	-1.332012	-1.099079
O	0.140330	-0.114644	1.625365	P	0.606159	-0.202262	-0.071543
O	0.282136	1.266861	-0.682426	O	0.344936	1.255090	-0.723720
C	-0.913821	2.045770	-0.517187	C	-0.720743	2.124219	-0.313819
Li	-0.689745	-1.886633	-1.282526	O	2.355398	0.047209	0.122549
Li	2.728007	-1.128134	-0.618212	O	0.373997	-0.307314	1.442408
O	2.305479	0.304977	0.363766	Li	2.098450	-0.199341	1.920617
H	-1.175695	2.135880	0.540787	H	-1.661589	1.784967	-0.748280
H	-1.736533	1.578845	-1.059890	H	-0.451959	3.116699	-0.683332

H	-0.683157	3.031927	-0.927249	H	-0.808864	2.145584	0.776481
H	-2.250872	-0.544097	1.519265	H	-3.411333	-1.167863	0.681990
H	-3.320753	-1.465282	0.431755	H	-3.086297	0.571868	0.745911
H	-3.240775	0.300133	0.305541	H	-2.090636	-0.547179	1.702486
H	2.444522	0.804103	1.176896	H	2.830468	-0.255402	-0.660695
D-Li2-Product				E-Li2-Product			
C	-4.059747	-0.156975	-0.017693	C	-2.956681	-0.297479	0.732322
O	-2.771919	-0.636521	0.075340	O	-2.185590	-0.522147	-0.391397
P	1.235948	0.015822	0.232217	Li	-1.212798	-1.524322	-1.314291
O	0.530385	-1.369537	0.079037	O	0.605953	-1.337247	-1.062804
O	1.591019	0.550129	1.568448	P	0.807486	-0.203430	-0.082839
O	0.571298	1.067907	-0.781296	O	0.500271	1.228165	-0.733236
C	-0.561096	1.882660	-0.345071	C	-0.583406	2.082713	-0.282922
Li	-1.340107	-1.406775	0.291191	O	2.511436	-0.089957	0.102938
Li	1.857789	-2.134684	-0.900187	O	0.480799	-0.280885	1.405390
O	2.598061	-0.413537	-0.683605	Li	2.180343	-0.301043	1.972392
H	-0.301165	2.407095	0.577683	H	-1.531847	1.599606	-0.526894
H	-1.442002	1.243347	-0.207507	H	-0.447456	3.024015	-0.818141
H	-0.725023	2.597305	-1.151658	H	-0.507802	2.246222	0.795816
H	-4.096999	0.937166	-0.210484	H	-3.892399	-0.892224	0.738604
H	-4.649802	-0.321609	0.906799	H	-3.278350	0.762699	0.825785
H	-4.635956	-0.628566	-0.840018	H	-2.421164	-0.538727	1.671998
H	3.332968	0.210669	-0.617887	H	3.001661	-0.368887	-0.682417
E-Na2-Reactant				E-K2-Reactant			
C	-1.580402	1.845461	1.183019	C	-1.533970	1.935246	1.441431
O	-1.828647	0.608380	0.496932	O	-1.789599	0.714496	0.735324
P	-0.509742	-0.294185	-0.082384	P	-0.472701	-0.094826	0.042785
O	0.030114	0.625623	-1.289137	O	-0.096861	0.928012	-1.159989
C	1.292851	1.353394	-1.251627	C	1.187210	1.603293	-1.252038
O	-1.250577	-1.487908	-0.654271	O	-1.155782	-1.315690	-0.538269
O	0.496462	-0.428939	1.032511	O	0.634978	-0.195854	1.059355
Na	-3.283111	-0.913662	-0.338630	K	-3.590785	-0.867308	-0.446309
Na	2.643241	-0.830677	1.053047	K	3.126840	-0.900516	0.823186
H	2.162087	0.694682	-1.113907	H	2.033687	0.907431	-1.341868
H	1.270304	2.105305	-0.456514	H	1.337870	2.250335	-0.381614
H	1.356657	1.852952	-2.219850	H	1.121890	2.218684	-2.152054
H	-2.533677	2.191324	1.589952	H	-2.470478	2.243013	1.915040
H	-1.191775	2.595830	0.486601	H	-1.205407	2.718883	0.749155
H	-0.867646	1.688691	1.997525	H	-0.769195	1.779415	2.208191
O	3.974259	-0.142617	-0.307903	O	4.073227	0.038564	-1.106113
H	4.841167	-0.117718	-0.720047	H	4.609961	0.305831	-1.858106
E-Na2-TS1				E-K2-TS1			
C	-1.901509	1.559072	1.136393	C	1.463126	1.870225	-1.447188
O	-1.715794	0.327874	0.449193	O	1.536863	0.619569	-0.785786
P	-0.058289	-0.134407	-0.005307	P	0.052017	0.015911	0.007575
O	0.040897	1.104894	-1.071107	O	0.157373	1.218247	1.139082
C	1.214287	1.912508	-1.226507	C	-0.977151	1.980635	1.550288
O	-0.486874	-1.478412	-0.603207	O	0.696392	-1.305889	0.429109
O	0.651208	0.098401	1.327393	O	-0.947567	0.274014	-1.115362
Na	-2.610374	-1.409936	-0.492707	K	3.137198	-1.102413	0.167994
O	2.068618	-0.747882	-0.815807	O	-1.737576	-0.728764	1.245919
Na	2.622418	-0.755176	1.184993	K	-3.174160	-0.781233	-0.691433
H	2.045495	1.293517	-1.570007	H	-1.710470	1.328046	2.029463

H	1.475182	2.396811	-0.276407	H	-1.436107	2.487244	0.690306
H	0.952179	2.680905	-1.960007	H	-0.599274	2.736297	2.246889
H	-2.959609	1.641460	1.412393	H	2.427992	2.061009	-1.936354
H	-1.635818	2.407675	0.492393	H	1.265742	2.684815	-0.735508
H	-1.286009	1.588679	2.042593	H	0.671287	1.865089	-2.205722
H	1.809326	-1.445185	-1.427507	H	-1.256890	-1.334486	1.820343
E-Na2-Intermidiate-1				E-K2-Intermidiate-1			
P	0.043193	-0.185109	-0.074497	P	0.033424	-0.020671	-0.092804
O	-0.573084	-1.418755	-0.781292	O	-0.729714	-1.226866	-0.690007
O	0.688955	-0.095931	1.325449	O	0.973113	0.041450	1.126347
O	0.044543	1.226243	-0.956946	O	-0.175677	1.427398	-0.918019
O	-1.642860	0.316584	0.516010	O	-1.482176	0.463786	0.866919
C	-1.744560	1.452305	1.349539	C	-1.372288	1.555612	1.750023
C	1.215740	2.010445	-1.145651	C	0.919953	2.234394	-1.319738
H	1.747588	2.167215	-0.197895	H	1.640038	2.370003	-0.500840
H	0.875637	2.980892	-1.522230	H	0.502561	3.213411	-1.582851
H	1.899380	1.546424	-1.861317	H	1.446047	1.806875	-2.178470
H	-2.792570	1.572702	1.658202	H	-2.340187	1.706398	2.253907
H	-1.434560	2.363796	0.817880	H	-1.119327	2.484357	1.214446
H	-1.119589	1.337502	2.243872	H	-0.601958	1.376421	2.511985
Na	2.629757	-0.922431	1.083937	K	3.173747	-0.905417	0.557681
Na	-2.668235	-1.232551	-0.517957	K	-3.138902	-1.021828	-0.245294
O	1.763888	-0.655241	-0.841521	O	1.529373	-0.433083	-1.247879
H	1.520864	-1.246797	-1.563763	H	1.104051	-0.951252	-1.942065
E-Na2-TS2 (-CH3 rotation)				E-K2-TS2 (-CH3 Rotation)			
C	-1.683457	1.488300	-1.418029	P	-0.026071	-0.066758	-0.022621
O	-1.590424	0.455396	-0.467801	O	-0.259148	0.140679	1.481725
Na	-2.563393	-1.320570	0.151531	O	-0.957382	-0.107834	-1.244221
O	-0.464343	-1.685707	0.135851	O	1.651896	-0.304889	-0.222748
P	0.156713	-0.279270	0.061935	O	0.355808	1.782801	-0.265701
O	-0.057886	0.480651	1.526204	C	-0.196199	2.491433	-1.344845
C	0.337310	1.834624	1.677771	C	2.119050	-0.811350	-1.462538
O	1.834842	-0.900284	0.649440	H	1.881455	-0.131110	-2.290820
O	0.848446	0.482943	-1.085195	H	3.207515	-0.911501	-1.385731
Na	2.868125	-0.198045	-1.058224	H	1.682835	-1.797105	-1.665993
H	-0.229053	2.497113	1.013402	H	0.139391	3.539714	-1.282035
H	0.131644	2.109687	2.716808	H	0.117236	2.093375	-2.323064
H	1.410740	1.963463	1.484978	H	-1.296507	2.482812	-1.334458
H	-2.747043	1.705687	-1.608565	K	-2.243809	-2.220304	-1.241860
H	-1.212150	2.422766	-1.075106	K	1.738451	1.682384	1.816201
H	-1.205085	1.221181	-2.370879	O	-0.192690	-1.963042	0.138323
H	1.659999	-1.627621	1.257512	H	0.136254	-2.151717	1.025550
E-Na2-Intermmidiate-2				E-K2-Intermidiate-2			
C	-1.853441	1.291296	-1.403415	P	0.097403	0.003068	-0.133247
O	-1.626399	0.297802	-0.440160	O	-0.515132	0.048976	-1.543759
Na	-2.358760	-1.623575	0.012535	O	1.182518	0.862395	0.534294
O	-0.255789	-1.702817	0.281263	O	-0.679808	-1.259869	0.710892
P	0.296121	-0.273782	0.134266	O	-1.306507	1.048413	0.630340
O	0.085542	0.644237	1.489963	C	-1.138084	2.444236	0.621432
C	-0.434574	1.967834	1.443170	C	-0.338311	-1.436687	2.078686
O	1.961824	-0.749162	0.728928	H	-0.529784	-0.521427	2.651050
O	0.868528	0.447133	-1.098892	H	-0.960614	-2.250049	2.468762
Na	2.961420	0.069867	-0.970396	H	0.717035	-1.720092	2.183276

H	-1.521919	1.957408	1.328147	H	-2.007603	2.913231	1.110191
H	-0.161777	2.437742	2.393401	H	-0.230491	2.746026	1.161528
H	0.003847	2.541717	0.618624	H	-1.065368	2.853730	-0.403620
H	-2.703726	1.022068	-2.056815	K	3.408357	0.193925	-0.306649
H	-2.103669	2.268772	-0.947232	K	-2.897478	-0.394800	-0.730800
H	-0.970041	1.436149	-2.039124	O	1.417013	-1.256614	-0.631590
H	1.844661	-1.518664	1.298134	H	0.982790	-1.842507	-1.263085
E-Na2-TS3				E-K2-TS3			
C	1.904420	1.319155	-1.366211	C	1.261299	2.538632	-0.276936
O	1.676116	0.306887	-0.428700	O	1.516597	1.213244	0.050549
Na	2.345233	-1.633525	-0.014439	P	-0.196417	-0.247863	-0.141871
O	0.236788	-1.712331	0.249714	O	-1.128303	0.948600	0.012546
P	-0.322830	-0.287117	0.140167	O	0.497424	-0.837925	-1.363126
O	-0.091476	0.601915	1.505503	O	0.556434	-0.849676	1.223735
C	0.431013	1.927144	1.479141	C	0.442127	-0.114828	2.443039
O	-1.986409	-0.753890	0.700794	O	-1.534440	-1.452062	-0.035674
O	-0.855083	0.471553	-1.084626	K	2.914218	-0.690666	-0.547935
Na	-2.956066	0.124187	-0.997276	K	-3.451166	0.180320	-0.336316
H	1.516303	1.912071	1.353289	H	0.816262	0.902270	2.296374
H	0.165427	2.378529	2.440178	H	1.049398	-0.641299	3.186733
H	-0.012708	2.515106	0.667853	H	-0.598709	-0.091088	2.790395
H	2.754264	1.070739	-2.030318	H	2.132159	3.183905	-0.039587
H	2.155012	2.288552	-0.889789	H	0.392395	2.951679	0.267061
H	1.021297	1.482760	-2.000328	H	1.043974	2.689453	-1.356518
H	-1.890071	-1.529157	1.266408	H	-1.169465	-2.300653	-0.316490
E-Na2-Product				E-K2-Product			
C	4.556328	0.592168	-0.043766	C	4.454084	1.584290	-0.061298
O	3.410261	-0.166644	-0.073399	O	3.709125	0.431725	-0.087067
Na	1.987031	-1.589720	-0.131278	K	2.607614	-1.642441	-0.181431
O	-0.177796	-1.355999	0.022547	O	0.067312	-1.367054	0.151757
P	-1.081712	-0.150150	0.004329	P	-0.943419	-0.251883	0.090727
O	-0.376690	1.160915	0.629249	O	-0.359160	1.138355	0.699117
C	0.781341	1.769611	-0.016917	C	0.732145	1.828764	0.029233
O	-2.291870	-0.341911	1.168231	O	-2.129174	-0.510002	1.262655
O	-1.923699	0.176985	-1.218488	O	-1.770863	0.003080	-1.155534
Na	-3.887782	0.187246	-0.357216	K	-4.104011	0.303638	-0.329475
H	1.659623	1.105601	0.008674	H	1.671004	1.255639	0.067298
H	0.983916	2.674581	0.557432	H	0.855135	2.768738	0.569657
H	0.525698	2.041927	-1.046026	H	0.453813	2.042252	-1.008665
H	5.173917	0.497839	-0.965278	H	5.098444	1.721316	-0.961737
H	5.236510	0.335214	0.799455	H	5.148300	1.649561	0.809668
H	4.353272	1.684216	0.064577	H	3.834653	2.515269	-0.006390
H	-1.946665	-0.617367	2.028645	H	-1.733811	-0.784411	2.101453