

SUPPORTING INFORMATION

THEORETICAL STUDY OF ACID-CATALYZED HYDROLYSIS OF EPOXIDES

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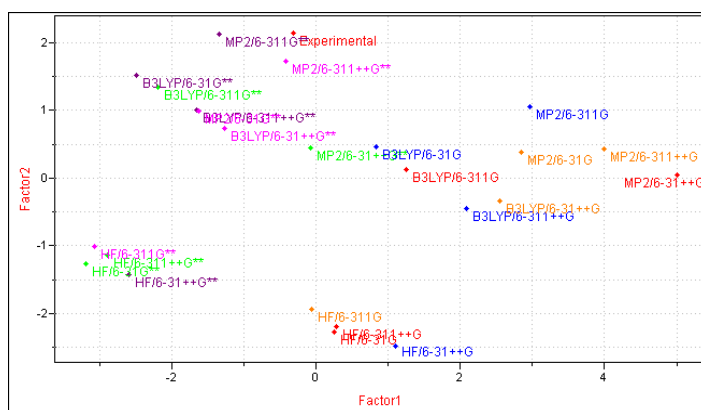
Table S1. Experimental and calculated internal coordinates values (r, bond lengths in Å; a, angles in degrees; d, dihedrals in degrees).

Method	Basis sets	Parameters								
		RCC	RCO	rCH	aCOC	aHCH	aHCC	aHCO	aCCO	dHCCO
HF	6-31G	1.463	1.459	1.071	60.17	115.63	119.81	114.51	59.91	102.75
	6-31G**	1.453	1.401	1.077	62.46	115.29	119.81	115.29	58.77	103.21
	6-31++G	1.464	1.463	1.071	60.06	115.91	119.78	114.22	59.97	102.42
	6-31++G**	1.454	1.403	1.077	62.43	115.50	119.79	115.08	58.78	102.96
	6-311G	1.463	1.452	1.069	60.51	115.75	119.70	114.61	59.74	102.84
	6-311G**	1.454	1.399	1.077	62.63	115.45	119.74	115.26	58.69	103.16
	6-311++G	1.463	1.453	1.069	60.46	115.83	119.72	114.47	59.77	102.67
	6-311++G**	1.454	1.400	1.077	62.59	115.49	119.75	115.19	58.70	103.07
B3LYP	6-31G	1.479	1.491	1.086	59.50	115.38	119.72	114.80	60.25	103.30
	6-31G**	1.469	1.430	1.090	61.80	115.18	119.65	115.53	59.10	103.73
	6-31++G	1.479	1.498	1.085	59.16	115.92	119.71	114.17	60.42	102.60
	6-31++G**	1.470	1.434	1.089	61.66	115.54	119.68	115.07	59.17	103.16
	6-311G	1.477	1.489	1.081	59.46	115.69	119.62	114.62	60.27	103.13
	6-311G**	1.467	1.429	1.087	61.77	115.41	119.57	115.40	59.11	103.61
	6-311++G	1.476	1.493	1.081	59.26	115.90	119.66	114.29	60.37	102.75
	6-311++G**	1.467	1.431	1.087	61.67	115.56	119.59	115.20	59.16	103.36
MP2	6-31G	1.485	1.524	1.087	58.31	115.62	119.70	114.34	60.84	103.01
	6-31G**	1.464	1.437	1.083	61.22	115.56	119.51	115.23	59.39	103.55
	6-31++G	1.487	1.537	1.087	57.84	116.33	119.60	113.63	61.08	102.29
	6-31++G**	1.466	1.444	1.083	61.00	116.05	119.50	114.69	59.50	102.93
	6-311G	1.483	1.515	1.083	58.60	116.13	119.42	114.30	60.70	103.01
	6-311G**	1.468	1.430	1.086	61.73	116.00	119.31	115.17	59.14	103.46
	6-311++G	1.482	1.522	1.083	58.29	116.38	119.46	113.91	60.85	102.59
	6-311++G**	1.468	1.434	1.086	61.58	116.30	119.31	114.83	59.21	103.07
Experimental ^a		1.4594(4)	1.4252(3)	1.0840(4)	61.59	116.75(7)	119.08	114.70	59.20	103.02

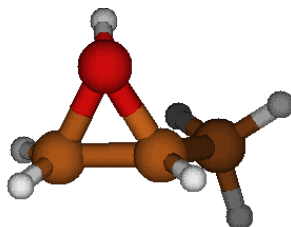
^aExperimental standard deviations are given in bracket

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Scores Plot from PCA analysis



Protonated Propylene Oxide - *syn*

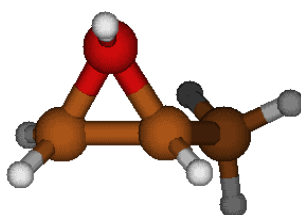


	1	2	3
Frequencies --	232.9376	345.7090	389.8171

Zero-point correction= 0.099611 (Hartree/Particle)
Thermal correction to Energy= 0.104196
Thermal correction to Enthalpy= 0.105141
Thermal correction to Gibbs Free Energy= 0.073066
Sum of electronic and zero-point Energies= -192.821405
Sum of electronic and thermal Energies= -192.816820
Sum of electronic and thermal Enthalpies= -192.815876
Sum of electronic and thermal Free Energies= -192.847950

C	-0.015137	0.006197	0.002295
C	-0.021892	0.004555	1.464837
H	0.956631	0.021267	-0.481048
H	0.906813	-0.041073	2.020201
H	-0.934663	-0.259266	1.989126
H	-1.043434	1.671750	0.774454
C	-1.204189	-0.370023	-0.814061
H	-1.253684	0.223227	-1.729363
H	-1.079137	-1.420799	-1.098871
H	-2.136104	-0.282305	-0.248696
O	-0.118814	1.353292	0.774157

Protonated Propylene Oxide – *anti*



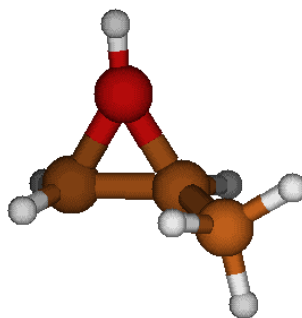
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	1	2	3
	A	A	A
Frequencies --	216.1634	351.4628	389.6781

Zero-point correction=	0.099561 (Hartree/Particle)
Thermal correction to Energy=	0.104171
Thermal correction to Enthalpy=	0.105115
Thermal correction to Gibbs Free Energy=	0.072982
Sum of electronic and zero-point Energies=	-192.821839
Sum of electronic and thermal Energies=	-192.817229
Sum of electronic and thermal Enthalpies=	-192.816284
Sum of electronic and thermal Free Energies=	-192.848417

C	1.250000	-0.241228	0.000000
C	2.751115	-0.241228	0.000000
H	0.713404	-0.551103	-0.913858
H	3.287676	-0.550995	-0.913888
H	3.287676	-0.550995	0.913888
H	2.000307	1.678275	-0.913944
C	0.501573	-0.673432	1.274620
H	-0.470187	-0.225731	1.286760
H	0.403590	-1.738867	1.286740
H	1.051304	-0.355995	2.135973
O	2.000530	1.058747	0.000000

Protonated Propylene Oxide – TS



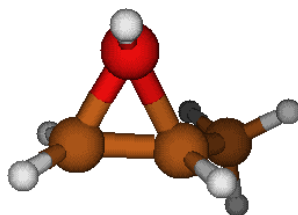
	1	2	3
	A	A	A
Frequencies --	-966.4011	230.0358	358.8166

Zero-point correction=	0.097231 (Hartree/Particle)
Thermal correction to Energy=	0.101799
Thermal correction to Enthalpy=	0.102743
Thermal correction to Gibbs Free Energy=	0.070693
Sum of electronic and zero-point Energies=	-192.796543
Sum of electronic and thermal Energies=	-192.791975
Sum of electronic and thermal Enthalpies=	-192.791031
Sum of electronic and thermal Free Energies=	-192.823081

C	-0.075068	0.000197	0.009397
C	-0.033655	-0.005085	1.496826
C	1.250986	0.006561	2.270789
O	0.494079	1.241048	2.144953
H	2.185258	0.029419	1.719575
H	1.267807	-0.376687	3.285224
H	0.479730	2.187919	2.373271
H	-0.913478	-0.337390	2.040824
H	-0.180304	-1.043141	-0.309512
H	0.840245	0.412191	-0.418328
H	-0.945668	0.551545	-0.351157

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S_N1 Mechanism – REAC

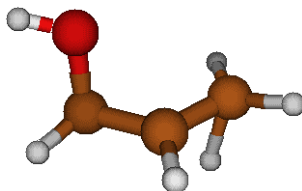


	1	2	3
	A	A	A
Frequencies --	216.1290	351.4302	389.6614

Zero-point correction= 0.099557 (Hartree/Particle)
Thermal correction to Energy= 0.104168
Thermal correction to Enthalpy= 0.105112
Thermal correction to Gibbs Free Energy= 0.072979
Sum of electronic and zero-point Energies= -192.821842
Sum of electronic and thermal Energies= -192.817231
Sum of electronic and thermal Enthalpies= -192.816287
Sum of electronic and thermal Free Energies= -192.848421

C	0.302805	0.397556	-0.294982
C	-0.819042	0.725055	0.585583
O	-0.929563	-0.557580	-0.218463
H	0.316078	0.888057	-1.265170
H	-1.548483	1.469924	0.286647
H	-0.762821	0.472587	1.637977
H	-1.524270	-0.438307	-0.984952
C	1.551548	-0.249996	0.188361
H	1.379686	-0.807074	1.110986
H	1.969075	-0.906108	-0.577210
H	2.273285	0.550645	0.386907

S_N1 Mechanism – TSI



	1	2	3
	A	A	A
Frequencies --	-148.6114	236.0642	269.6965

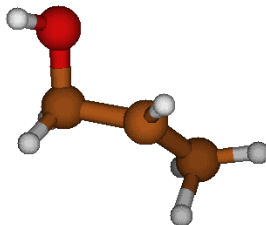
Zero-point correction= 0.095193 (Hartree/Particle)
Thermal correction to Energy= 0.099864
Thermal correction to Enthalpy= 0.100809
Thermal correction to Gibbs Free Energy= 0.068412
Sum of electronic and zero-point Energies= -192.796717
Sum of electronic and thermal Energies= -192.792046
Sum of electronic and thermal Enthalpies= -192.791102
Sum of electronic and thermal Free Energies= -192.823499

C	-0.483142	0.156171	0.639891
C	0.839547	0.446021	-0.037241
O	1.195553	-0.851985	-0.476107
H	-0.568367	0.185209	1.727215
H	1.543251	0.868094	0.683201
H	0.704031	1.145589	-0.871617
H	2.156549	-0.919571	-0.517436

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C	-1.602248	-0.208327	-0.102120
H	-1.528485	-0.274504	-1.185821
H	-2.505644	-0.554577	0.394904
H	-1.522596	0.999704	0.190401

S_N1 Mechanism – TS2

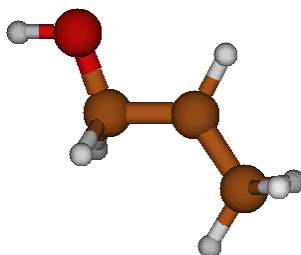


	1	2	3
	A	A	A
Frequencies --	-204.4567	154.5427	205.8634

Zero-point correction=	0.094225 (Hartree/Particle)
Thermal correction to Energy=	0.099485
Thermal correction to Enthalpy=	0.100429
Thermal correction to Gibbs Free Energy=	0.066793
Sum of electronic and zero-point Energies=	-192.797935
Sum of electronic and thermal Energies=	-192.792675
Sum of electronic and thermal Enthalpies=	-192.791731
Sum of electronic and thermal Free Energies=	-192.825368

C	0.001579	0.074867	0.030055
C	0.031642	0.123943	1.520647
C	1.183872	0.018188	2.336765
O	-0.739942	1.236255	-0.278339
H	-0.948169	0.206130	1.997408
H	-0.490174	-0.863637	-0.265557
H	1.002177	0.115709	-0.407608
H	-1.486536	1.015858	-0.847489
H	2.153785	0.137497	1.858679
H	0.971394	-1.110329	2.385129
H	1.096400	0.356598	3.368664

S_N1 Mechanism – TS3



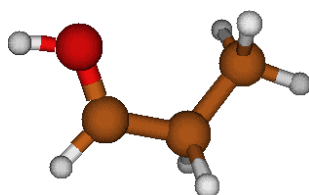
	1	2	3
	A	A	A
Frequencies --	-177.8162	125.7682	160.7679

Zero-point correction=	0.093209 (Hartree/Particle)
Thermal correction to Energy=	0.098623
Thermal correction to Enthalpy=	0.099567
Thermal correction to Gibbs Free Energy=	0.065536
Sum of electronic and zero-point Energies=	-192.807506
Sum of electronic and thermal Energies=	-192.802092
Sum of electronic and thermal Enthalpies=	-192.801148
Sum of electronic and thermal Free Energies=	-192.835179

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C	0.007847	-0.000002	-0.000517
C	-0.005322	0.000034	1.441301
C	1.182575	0.000007	2.266844
O	0.855027	0.000041	3.611239
H	1.775736	-0.874582	1.915599
H	1.775798	0.874540	1.915565
H	-0.970902	0.000082	1.958236
H	-0.602888	0.860529	-0.329090
H	0.994641	-0.000050	-0.459236
H	-0.602953	-0.860502	-0.329050
H	1.656135	0.000088	4.146112

S_N1 Mechanism – *PROD1*

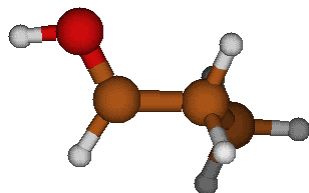


	1	2	3
	A	A	A
Frequencies --	115.9638	236.3992	251.6764

Zero-point correction=	0.098374 (Hartree/Particle)
Thermal correction to Energy=	0.103533
Thermal correction to Enthalpy=	0.104477
Thermal correction to Gibbs Free Energy=	0.070867
Sum of electronic and zero-point Energies=	-192.852628
Sum of electronic and thermal Energies=	-192.847470
Sum of electronic and thermal Enthalpies=	-192.846526
Sum of electronic and thermal Free Energies=	-192.880136

C	0.450191	0.707028	-0.273396
C	-0.884064	0.541569	0.283499
O	-1.193261	-0.522697	0.896909
H	0.809655	1.662733	0.148934
H	0.277415	0.962661	-1.334390
H	-1.641289	1.325396	0.185186
H	-2.112335	-0.527782	1.229127
C	1.422957	-0.449683	-0.076507
H	1.047951	-1.362470	-0.543223
H	2.375970	-0.193106	-0.539586
H	1.596007	-0.641605	0.984083

S_N1 Mechanism – *PROD2*



	1	2	3
	A	A	A
Frequencies --	85.7810	210.0125	303.8268

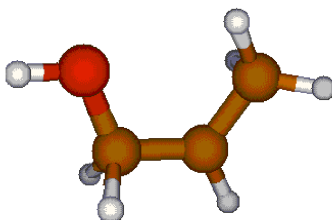
Zero-point correction=	0.099083 (Hartree/Particle)
Thermal correction to Energy=	0.104258

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Thermal correction to Enthalpy= 0.105202
Thermal correction to Gibbs Free Energy= 0.071369
Sum of electronic and zero-point Energies= -192.851314
Sum of electronic and thermal Energies= -192.846138
Sum of electronic and thermal Enthalpies= -192.845194
Sum of electronic and thermal Free Energies= -192.879027

C	-0.089227	0.101666	-0.009814
C	-0.042411	-0.652652	1.229583
C	1.060881	0.014728	2.116719
O	-1.063918	0.876901	-0.247632
H	-1.014161	-0.644270	1.724839
H	0.273296	-1.675464	0.994907
H	0.733306	0.063275	-0.730752
H	-0.967887	1.379267	-1.080241
H	2.035265	0.004835	1.623936
H	1.129215	-0.571836	3.033756
H	0.784375	1.039022	2.371673

S_N1 Mechanism – PROD_Carbocation (obtained by HF/6-311++G** method)



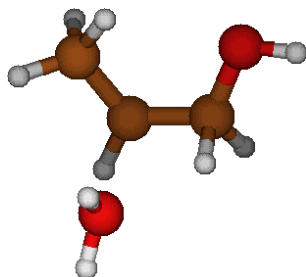
	1	2	3
	A	A	A
Frequencies --	145.8458	188.2979	293.9724

Zero-point correction= 0.099772 (Hartree/Particle)
Thermal correction to Energy= 0.105226
Thermal correction to Enthalpy= 0.106171
Thermal correction to Gibbs Free Energy= 0.072147
Sum of electronic and zero-point Energies= -192.188894
Sum of electronic and thermal Energies= -192.183440
Sum of electronic and thermal Enthalpies= -192.182496
Sum of electronic and thermal Free Energies= -192.216520

C	0.641433	0.641243	-0.018192
C	-0.809542	0.570091	0.120913
O	-1.228223	-0.721016	0.288132
H	1.043161	1.630074	-0.195612
H	-1.230441	1.077572	-0.754599
H	-1.024532	1.234722	0.971358
H	-2.163633	-0.782903	0.397901
C	1.539882	-0.490558	0.007618
H	1.135598	-1.344040	0.531681
H	1.564400	-0.756295	-1.066783
H	2.549512	-0.224439	0.289219

S_N1 Mechanism – TS (Carbocation+H₂O)

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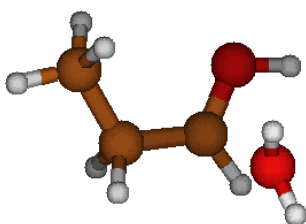


	1	2	3
	A	A	A
Frequencies --	-393.4833	75.4849	93.5624

Zero-point correction= 0.118590 (Hartree/Particle)
Thermal correction to Energy= 0.127021
Thermal correction to Enthalpy= 0.127965
Thermal correction to Gibbs Free Energy= 0.086430
Sum of electronic and zero-point Energies= -269.087175
Sum of electronic and thermal Energies= -269.078744
Sum of electronic and thermal Enthalpies= -269.077800
Sum of electronic and thermal Free Energies= -269.119335

C	0.123219	-0.224856	0.058344
C	0.103298	-0.153875	1.483315
O	1.344510	-0.252769	2.073758
H	-0.848010	-0.277187	-0.432278
H	-0.728099	-0.689040	1.958255
H	-0.275540	0.922257	1.362989
H	1.273351	-0.046148	3.012139
H	-1.303969	2.727102	-0.681956
H	0.165815	3.050910	-0.538038
O	-0.470510	2.343076	-0.387659
C	1.333659	-0.223348	-0.734480
H	1.517107	-1.319765	-0.819941
H	1.194680	0.167990	-1.740177
H	2.193020	0.180736	-0.199347

S_N1 Mechanism – PROD (Carbocation+H₂O)



	1	2	3
	A	A	A
Frequencies --	36.1830	104.5172	156.2465

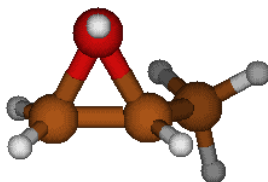
Zero-point correction= 0.124548 (Hartree/Particle)
Thermal correction to Energy= 0.132953
Thermal correction to Enthalpy= 0.133897
Thermal correction to Gibbs Free Energy= 0.091940
Sum of electronic and zero-point Energies= -269.013881
Sum of electronic and thermal Energies= -269.005476
Sum of electronic and thermal Enthalpies= -269.004531

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Sum of electronic and thermal Free Energies= -269.046489

C	0.043732	0.817461	0.826937
C	-0.330781	-0.570478	0.577407
O	-1.142922	-0.843711	-0.367053
H	-0.413485	1.039560	1.804529
H	-0.009443	-1.371022	1.235427
H	1.118802	0.806637	1.029869
H	-1.334736	-1.800183	-0.444830
H	2.379162	-2.044105	-0.245756
H	1.866872	-1.341678	-1.508301
O	1.624700	-1.548744	-0.594690
C	-0.360750	1.823946	-0.240787
H	-1.438332	1.839204	-0.386534
H	-0.044270	2.815903	0.070417
H	0.118062	1.596235	-1.191080

Pure S_N2 Mechanism – REAC



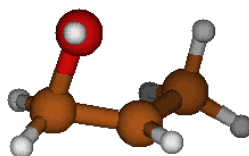
	1	2	3
	A	A	A
Frequencies --	62.1155	81.3320	138.5976

Zero-point correction= 0.123623 (Hartree/Particle)
Thermal correction to Energy= 0.131877
Thermal correction to Enthalpy= 0.132821
Thermal correction to Gibbs Free Energy= 0.091389
Sum of electronic and zero-point Energies= -269.093459
Sum of electronic and thermal Energies= -269.085205
Sum of electronic and thermal Enthalpies= -269.084261
Sum of electronic and thermal Free Energies= -269.125693

C	0.364037	-0.028368	-0.020651
C	-0.214590	-0.094689	1.310002
O	1.304774	0.126418	1.225873
H	0.570128	-0.977361	-0.508614
H	-0.466161	-1.051175	1.750371
H	-0.663508	0.790021	1.741638
H	1.781655	-0.704983	1.409660
H	-3.045692	-1.194984	-0.068517
H	-3.269960	0.286103	0.092061
O	-2.571562	-0.376548	0.112069
C	0.333011	1.200590	-0.856196
H	1.218916	1.265113	-1.490074
H	-0.552263	1.120878	-1.495744
H	0.246233	2.096782	-0.239184

Pure S_N2 Mechanism – TS

SUPPORTING INFORMATION

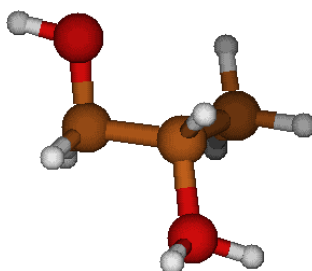


	1	2	3
	A	A	A
Frequencies --	-366.5813	107.6644	130.5849

Zero-point correction= 0.122466 (Hartree/Particle)
Thermal correction to Energy= 0.130195
Thermal correction to Enthalpy= 0.131140
Thermal correction to Gibbs Free Energy= 0.091551
Sum of electronic and zero-point Energies= -269.084020
Sum of electronic and thermal Energies= -269.076291
Sum of electronic and thermal Enthalpies= -269.075347
Sum of electronic and thermal Free Energies= -269.114935

C	-0.087272	-0.054135	0.005297
C	0.027154	-0.032313	1.466097
O	1.455650	-0.036531	1.181322
H	0.026954	-1.023040	-0.472367
H	-0.315189	-0.915638	1.998866
H	-0.244411	0.898679	1.956216
H	1.817946	-0.920571	1.345640
H	-2.695370	-1.117533	-0.174818
H	-2.812638	0.375891	-0.496393
O	-2.233471	-0.275201	-0.081474
C	0.021717	1.168584	-0.819335
H	1.087929	1.350270	-1.002388
H	-0.447581	1.008933	-1.791180
H	-0.398357	2.037961	-0.311756

Pure S_N2 Mechanism – *PROD*



	1	2	3
	A	A	A
Frequencies --	61.9911	187.8384	196.2558

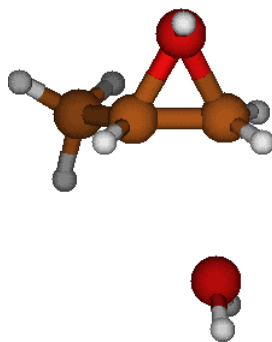
Zero-point correction= 0.126735 (Hartree/Particle)
Thermal correction to Energy= 0.133868
Thermal correction to Enthalpy= 0.134812
Thermal correction to Gibbs Free Energy= 0.096287
Sum of electronic and zero-point Energies= -269.101223

SUPPORTING INFORMATION

Sum of electronic and thermal Energies= -269.094090
Sum of electronic and thermal Enthalpies= -269.093146
Sum of electronic and thermal Free Energies= -269.131671

C	-0.428864	-0.084500	-0.137485
C	0.065045	-0.196788	1.296806
O	1.457762	-0.329298	1.130873
H	-0.193038	-0.982085	-0.711536
H	-0.380035	-1.076623	1.782426
H	-0.214475	0.705788	1.853824
H	1.868042	-0.436909	1.995465
H	-2.364020	-0.944620	0.235526
H	-2.419189	0.237437	-0.822470
O	-1.978845	-0.084509	-0.014463
C	-0.069438	1.190438	-0.843375
H	1.022678	1.225190	-0.888022
H	-0.447759	1.216116	-1.869387
H	-0.418842	2.061551	-0.283188

Borderline S_N2 Mechanism – REAC



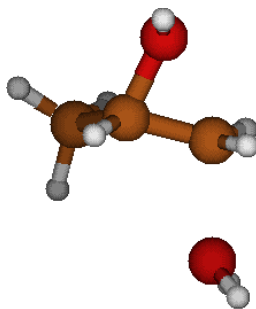
	1	2	3
	A	A	A
Frequencies --	62.1428	81.3086	138.1094

Zero-point correction= 0.123621 (Hartree/Particle)
Thermal correction to Energy= 0.131877
Thermal correction to Enthalpy= 0.132821
Thermal correction to Gibbs Free Energy= 0.091385
Sum of electronic and zero-point Energies= -269.093461
Sum of electronic and thermal Energies= -269.085205
Sum of electronic and thermal Enthalpies= -269.084261
Sum of electronic and thermal Free Energies= -269.125697

C	0.108188	0.015547	-0.025649
C	0.017735	-0.000729	1.423963
O	1.435247	-0.010686	0.750649
O	-2.548190	0.129177	-0.044082
C	-0.209892	1.224388	2.234337
H	-0.052442	-0.891608	-0.594275
H	0.042041	0.957299	-0.554109
H	-0.164347	-0.966235	1.888516
H	1.814919	-0.909720	0.747852
H	-3.167477	-0.600201	-0.152342
H	-3.072082	0.896254	-0.297812
H	-1.290406	1.294174	2.397729
H	0.287215	1.150632	3.202963
H	0.128030	2.117400	1.705459

Borderline S_N2 Mechanism – TS

SUPPORTING INFORMATION

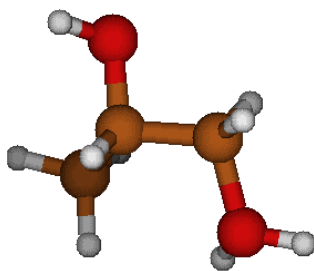


	1	2	3
	A	A	A
Frequencies --	-476.0647	71.4108	159.9373

Zero-point correction= 0.123651 (Hartree/Particle)
Thermal correction to Energy= 0.130821
Thermal correction to Enthalpy= 0.131765
Thermal correction to Gibbs Free Energy= 0.093181
Sum of electronic and zero-point Energies= -269.080914
Sum of electronic and thermal Energies= -269.073744
Sum of electronic and thermal Enthalpies= -269.072800
Sum of electronic and thermal Free Energies= -269.111384

C	-0.100663	-0.005661	-0.020174
C	-0.009816	0.033847	1.441890
O	1.418815	0.003494	1.085427
H	-0.000574	-0.953350	-0.535180
H	0.127854	0.901219	-0.566422
H	-0.317698	-0.883618	1.941977
H	1.773588	-0.891097	1.211588
H	-2.477604	-0.604580	-0.884852
H	-2.395981	0.930092	-0.777413
O	-2.041189	0.111854	-0.403993
C	-0.365566	1.295511	2.170581
H	-1.453509	1.376235	2.242887
H	0.050358	1.269016	3.179578
H	0.033386	2.166916	1.645763

Borderline S_N2 Mechanism – *PROD*



	1	2	3
	A	A	A
Frequencies --	117.4527	171.5406	194.5814

Zero-point correction= 0.127044 (Hartree/Particle)
Thermal correction to Energy= 0.134017
Thermal correction to Enthalpy= 0.134961
Thermal correction to Gibbs Free Energy= 0.097094
Sum of electronic and zero-point Energies= -269.096165
Sum of electronic and thermal Energies= -269.089191

SUPPORTING INFORMATION

Sum of electronic and thermal Enthalpies= -269.088247
Sum of electronic and thermal Free Energies= -269.126114

C	0.018010	-0.128134	-0.090711
C	0.066733	-0.073742	1.429762
O	1.469577	-0.054562	1.623149
O	-1.433812	0.056702	-0.525945
C	-0.607329	1.167836	1.999766
H	0.284028	-1.100647	-0.498546
H	0.591430	0.684033	-0.538448
H	-0.387208	-0.984188	1.837464
H	1.687455	-0.509080	2.443828
H	-1.568562	-0.011759	-1.488975
H	-1.815814	0.894881	-0.204167
H	-1.700375	1.132481	1.899435
H	-0.404427	1.230420	3.071112
H	-0.207549	2.074251	1.533020