Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Kinetics of the Benzyl + O(^3P) Reaction: A Quantum Chemical / Statistical Reaction Rate Theory Study

Supporting Information

Gabriel da Silva,* Joseph W. Bozzelli

gdasilva@unimelb.edu.au

Optimized Geometries (B3LYP/6-31G(2df,p), Å)

benzyl

C	0.000000	0.000000	-1.835740
C	0.000000	1.209190	-1.131080
C	0.000000	1.215500	0.251346
C	0.000000	0.000000	0.993474
C	0.000000	-1.215500	0.251346
C	0.000000	-1.209190	-1.131080
H	0.000000	0.000000	-2.920240
H	0.000000	2.149410	-1.673350
H	0.000000	2.156380	0.793098
H	0.000000	-2.156380	0.793098
H	0.000000	-2.149410	-1.673350
C	0.000000	0.000000	2.396260
H	0.000000	-0.927331	2.956790
H	0.000000	0.927331	2.956790

***o* 1**

C	-1.877890	-0.597008	-0.104274
C	-0.793679	-1.377990	-0.016903
C	0.575090	-0.795465	0.266375
C	0.672426	0.725208	0.053858
C	-0.580212	1.468790	0.048351
C	-1.777750	0.854054	-0.011149
H	-2.856050	-1.036950	-0.273937
H	-0.837319	-2.458450	-0.101273
H	-0.513619	2.552950	0.040306
H	-2.691020	1.438750	-0.043442
C	1.865340	1.314610	-0.098825
H	2.777370	0.730541	-0.123163
H	1.949130	2.389670	-0.217351
H	0.704344	-0.941551	1.377560
O	1.620910	-1.528510	-0.185412

***o* 2**

C	-1.968550	-0.347551	-0.000089
C	-0.869793	-1.361030	0.000042
C	0.563080	-0.824105	-0.000011
C	0.759636	0.669129	0.000015
C	-0.391461	1.500980	0.000131
C	-1.706570	0.990723	-0.000047
H	-2.991260	-0.710873	-0.000189
H	-0.956718	-2.032720	-0.866462
H	-0.241697	2.576700	0.000325
H	-2.531140	1.697270	-0.000113
C	2.041450	1.140880	-0.000112
H	2.872360	0.447052	-0.000099
H	2.252190	2.204550	-0.000044
H	-0.956696	-2.032370	0.866827
O	1.498280	-1.595480	0.000023

***o* 3**

C	1.872380	-0.689077	0.000046
C	0.656993	-1.377630	0.000001
C	-0.544735	-0.686619	0.000043
C	-0.575027	0.745023	0.000002
C	0.686609	1.405540	-0.000044
C	1.880160	0.710045	-0.000019
H	2.803600	-1.244540	0.000089
H	0.646203	-2.465080	-0.000026
H	0.687333	2.491190	-0.000094
H	2.821970	1.247800	-0.000045
C	-1.782960	1.449060	0.000062
H	-2.733680	0.935221	0.000204
H	-1.785030	2.532390	-0.000037
O	-1.749660	-1.320360	-0.000119
H	-1.603610	-2.272130	0.000323

***o*-QM**

C	1.862320	-0.575322	0.000017
C	0.777652	-1.380100	-0.000006
C	-0.582769	-0.829825	-0.000044
C	-0.681063	0.680615	-0.000011
C	0.541462	1.466160	-0.000010
C	1.751670	0.870508	0.000003
H	2.857970	-1.010340	0.000049
H	0.857166	-2.461460	0.000005
H	0.449977	2.548400	-0.000023
H	2.660470	1.462080	0.000002
C	-1.902190	1.244390	0.000016
H	-2.785370	0.615413	0.000014
H	-2.035300	2.321280	0.000041
O	-1.575920	-1.541740	0.000015

TS*o* 1

C	-1.906050	-0.555622	-0.053372
C	-0.798152	-1.362330	-0.043079
C	0.600205	-0.806303	0.086008
C	0.681585	0.711147	0.022885
C	-0.549405	1.461720	0.021075
C	-1.775850	0.864467	-0.016448
H	-2.892640	-1.003200	-0.112615
H	-0.852406	-2.445580	-0.051347
H	-0.474890	2.545600	0.007957
H	-2.673450	1.473260	-0.030980
C	1.899970	1.298350	-0.037228
H	2.793220	0.686031	-0.054719
H	2.007270	2.376770	-0.075383
H	0.170911	-0.995127	1.208200
O	1.626020	-1.538300	-0.096270

TS*o* 2

C	-1.876610	-0.459232	-0.081705
C	-0.823949	-1.316330	-0.050210
C	0.563156	-0.821205	-0.067146
C	0.723844	0.681082	0.008227
C	-0.463591	1.516080	0.003365
C	-1.700540	0.973965	-0.047879
H	-2.888830	-0.851312	-0.121674
H	-0.950159	-2.390550	-0.117676
H	-0.327175	2.593080	0.035034
H	-2.580810	1.607180	-0.058534
C	1.967170	1.190890	0.077136
H	2.823090	0.525381	0.076918
H	2.144240	2.259850	0.134097
H	-0.734969	-1.769760	2.214330
O	1.522210	-1.570670	-0.151653

TS*o* 3

C	-1.866140	-0.677638	-0.060282
C	-0.707224	-1.392910	-0.073947
C	0.579353	-0.736168	0.085287
C	0.606235	0.748543	0.015018
C	-0.666134	1.431030	0.054898
C	-1.844980	0.753782	0.025516
H	-2.820400	-1.189710	-0.128004
H	-0.697641	-2.475070	-0.146227
H	-0.653369	2.516680	0.071239
H	-2.785030	1.294790	0.040706
C	1.790170	1.411100	-0.089368
H	2.723070	0.864778	-0.143072
H	1.823050	2.493960	-0.130941
H	1.058590	-1.155010	1.108480
O	1.750500	-1.447110	-0.051865

TS*o* 4

C	-0.714410	1.426790	0.028401
C	-1.871390	0.729960	0.045321
C	-1.856530	-0.715497	0.016194
C	-0.701045	-1.421090	-0.021282
C	0.592582	-0.751278	-0.055883
C	0.567862	0.749275	-0.032950
H	-0.714279	2.512440	0.051832
H	-2.826290	1.242330	0.083152
H	-0.684614	-2.504920	-0.036360
C	1.737240	1.420320	-0.066147
H	2.674190	0.880571	-0.134152
H	1.770150	2.504350	-0.028821
O	1.652260	-1.385250	-0.094058
H	2.845170	-0.944753	1.303770
H	-2.808260	-1.238980	0.031109

***p* 1**

C	-1.483270	0.000036	0.270161
C	-0.664999	1.261950	0.141744
C	0.665326	1.243720	0.012179
C	1.436080	-0.000018	-0.027959
C	0.665304	-1.243750	0.012175
C	-0.665006	-1.261920	0.141773
H	-1.924910	-0.000042	1.305320
H	-1.226410	2.190790	0.148220
H	1.218780	-2.174290	-0.081754
H	-1.226570	-2.190670	0.148307
C	2.777530	-0.000009	-0.119147
H	3.343440	0.924363	-0.157820
H	3.343460	-0.924372	-0.157852
H	1.218850	2.174250	-0.081639
O	-2.641550	-0.000013	-0.463541

***p* 2**

C	1.507960	-0.058235	0.000001
C	0.769114	1.281430	0.000187
C	-0.721439	1.220210	-0.000079
C	-1.432650	0.017547	-0.000045
C	-0.660336	-1.232050	0.000035
C	0.683186	-1.276410	0.000149
H	1.136400	1.853020	-0.865769
H	1.135980	1.852460	0.866724
H	-1.231040	-2.157630	0.000015
H	1.225700	-2.216070	0.000209
C	-2.816910	-0.044946	-0.000067
H	-3.419690	0.855737	-0.000116
H	-3.337840	-0.994867	-0.000080
H	-1.268670	2.158500	-0.000195
O	2.723210	-0.099546	-0.000234

***p* 3**

C	-1.375530	0.018822	-0.000261
C	-0.660071	1.225090	-0.000087
C	0.718015	1.210700	0.000179
C	1.458590	-0.008595	0.000045
C	0.699378	-1.212680	-0.000043
C	-0.682275	-1.198250	-0.000031
H	-1.214280	2.156940	-0.000169
H	1.224730	-2.162510	0.000127
H	-1.236660	-2.133710	0.000178
C	2.859570	-0.019430	-0.000026
H	3.427010	0.903349	0.000008
H	3.413400	-0.950554	-0.000101
O	-2.735520	0.092756	0.000012
H	-3.099360	-0.798886	0.000976
H	1.263250	2.149370	0.000237

***p* -QM**

C	0.000000	0.000000	1.487680
C	0.000000	1.252010	0.703913
C	0.000000	1.245190	-0.640100
C	0.000000	0.000000	-1.400460
C	0.000000	-1.245190	-0.640100
C	0.000000	-1.252010	0.703913
H	0.000000	2.173240	1.276740
H	0.000000	-2.174420	-1.203610
H	0.000000	-2.173240	1.276740
C	0.000000	0.000000	-2.748640
H	0.000000	0.925125	-3.314770
H	0.000000	-0.925125	-3.314770
H	0.000000	2.174420	-1.203610
O	0.000000	0.000000	2.710760

TS*p* 1

C	-1.500810	0.017020	0.071414
C	-0.673711	1.257810	0.032482
C	0.670647	1.237030	-0.008442
C	1.442430	-0.000872	-0.017850
C	0.691090	-1.231880	-0.026299
C	-0.675657	-1.250170	-0.005520
H	-1.269170	-0.443539	1.196620
H	-1.231980	2.187890	0.013485
H	1.236480	-2.169690	-0.073354
H	-1.252960	-2.168420	-0.015209
C	2.804840	0.008678	-0.021030
H	3.362650	0.937904	-0.017335
H	3.376140	-0.912441	-0.030968
H	1.228320	2.168920	-0.047005
O	-2.750310	0.021710	-0.146845

TS*p* 2

C	-1.473140	0.051528	-0.045431
C	-0.669685	1.286610	0.052795
C	0.673866	1.258430	0.062935
C	1.419410	0.005973	-0.021619
C	0.648897	-1.224400	-0.096451
C	-0.704429	-1.218950	-0.053727
H	-1.065550	-1.570970	2.043450
H	-1.228360	2.215160	0.100559
H	1.198010	-2.159160	-0.165567
H	-1.286790	-2.126750	-0.164676
C	2.769370	-0.006840	-0.033378
H	3.345480	0.910358	0.022002
H	3.326850	-0.934838	-0.099152
H	1.249880	2.177760	0.124786
O	-2.690650	0.071797	-0.131518

TS*p* 3

C	-0.695463	-1.233830	-0.017842
C	0.657293	-1.240620	-0.001978
C	1.419810	0.000000	0.080483
C	0.657293	1.240620	-0.001978
C	-0.695463	1.233830	-0.017842
C	-1.458330	0.000000	-0.006408
H	-1.246000	-2.169390	-0.052653
H	1.224400	-2.165010	-0.029845
H	-1.246000	2.169390	-0.052653
H	2.140040	0.000000	1.058800
O	2.784970	0.000000	-0.140423
H	1.224400	2.165010	-0.029845
C	-2.819620	0.000000	0.002176
H	-3.384910	0.925066	0.004961
H	-3.384910	-0.925066	0.004961

TS*p* 4

C	-0.704672	-1.242730	-0.001467
C	0.642189	-1.246910	-0.035983
C	1.412820	0.000000	-0.070125
C	0.642189	1.246910	-0.035982
C	-0.704672	1.242730	-0.001467
C	-1.463920	0.000000	0.015885
H	-1.264840	-2.173450	0.015245
H	1.215150	-2.167860	-0.048395
H	-1.264840	2.173450	0.015245
H	3.595370	-0.000001	1.416600
O	2.651530	0.000000	-0.125423
H	1.215150	2.167860	-0.048395
C	-2.814820	0.000000	0.049806
H	-3.381460	0.924650	0.064541
H	-3.381460	-0.924650	0.064541

TS*p* 5

C	0.664145	1.247060	-0.010311
C	-0.673290	1.261510	0.024949
C	-1.474160	0.000000	0.027579
C	-0.673284	-1.261510	0.024953
C	0.664151	-1.247050	-0.010314
C	1.424220	-0.000002	-0.020874
H	1.229340	2.174150	-0.036053
H	-1.250000	2.179670	0.024136
H	1.229350	-2.174150	-0.036066
H	-1.348970	-0.000007	1.661930
O	-2.682140	-0.000002	-0.189956
H	-1.249990	-2.179670	0.024143
C	2.766020	0.000001	-0.039734
H	3.330260	-0.925787	-0.047968
H	3.330250	0.925793	-0.047967

NB: M06-2X/6-31G(2df,p) level

Vibrational Frequencies (B3LYP/6-31G(2df,p), cm^{-1})
(bold frequencies treated as hindered rotors)

benzyl

3254.01	3199.65	3185.71	3180.87	3168.22
3165.98	3156.24	1596.81	1574.66	1501.98
1493.06	1471.11	1346.74	1331.17	1291.01
1186.37	1175.23	1117.04	1037.53	992.11
980.569	972.472	949.523	894.765	840.679
830.771	780.927	711.852	688.647	623.426
530.289	507.233	482.657	390.489	355.333
202.483				

***o* 1**

3249.23	3199.9	3191.34	3170.46	3164.29
3156.09	2695.75	1700.81	1656.17	1615.63
1456.34	1410.56	1378.38	1301.81	1202.67
1179.41	1142.36	1100.77	1068.94	1029.77
989.694	984.089	973.421	944.83	934.783
857.861	837.266	786.72	736.454	676.36
665.407	558.698	478.47	459.741	423.818
382.788	315.104	217.527	67.2528	

***o* 2**

3264.69	3189.31	3173.5	3163.91	3159.47
3027.83	3008.64	1782.96	1576.53	1520.78
1443.35	1422.66	1403.8	1358.02	1335.95
1293.79	1183.73	1181.2	1143.06	1093.11
978.102	963.357	947.373	935.796	886.858
865.532	834.432	699.334	685.749	629.995
603.901	521.014	516.671	465.771	445.562
353.39	335.652	153.121	21.6781	

***o* 3**

3820.6	3276.85	3200.98	3185.89	3173.04
3169.19	3149.09	1600.3	1581.54	1505.53
1493.14	1474.08	1362.35	1324.84	1299.84
1285.83	1182.5	1173.99	1131.27	1056.68
972.08	945.168	894.165	866.898	851.69
768.108	761.308	751.971	706.438	588.913
563.712	522.196	500.331	440.996	438.303
389.787	323.202	275.436	159.91	

***o*-QM**

3252.04	3203.47	3196.21	3170.01	3164.8
3154.11	1743.42	1679.34	1633.81	1593.05
1460.36	1421.63	1376.49	1324.92	1209.54
1180.19	1149.01	1013.51	1004.98	997.912
971.35	951.066	889.221	876.998	821.859
773.59	711.485	674.698	572.279	522.979
471.301	441.557	435.256	335.899	234.604
92.4664				

TS*o* 1

3259.16	3206.33	3194.63	3178.41	3164.85
3157.81	2010.83	1603.52	1575.07	1494.02
1472.97	1425.52	1381.73	1336.06	1288.49
1181.89	1171.86	1078.52	1006.05	989.632
974.02	953.741	927.646	913.723	872.441
859.562	799.394	760.922	687.809	661.455
562.816	504.032	500.54	449.916	409.164
318.559	270.793	115.857		

TS*o* 2

3253.19	3208.12	3196.95	3172.14	3167.13
3154.86	1745.72	1663.83	1628.72	1549.77
1462.07	1420.71	1376.52	1322.64	1204.82
1179.72	1142.97	1005.72	1003.26	1001.25
970.606	952.515	887.347	876.581	819.993
781.483	710.32	674.168	570.947	524.563
476.123	442.421	436.796	335.488	257.495
219.413	161.598	92.4057		

TS*o* 3

3263.76	3202.17	3193.3	3178.1	3169.44
3162.19	2381.61	1637.69	1561.5	1494.78
1466.73	1427.04	1381.56	1317.32	1226.05
1209.33	1174.66	1137.22	1015.2	976.162
957.62	953.248	894.512	862.187	854.131
793.333	776.304	722.245	708.633	638.804
572.038	505.932	475.354	447.364	416.648
316.815	246.09	125.219		

TS*o* 4

3256.79	3205.62	3197.79	3172.87	3167.59
3156.66	1695.75	1651.23	1595.8	1556.88
1464.11	1425.21	1378.42	1327.69	1215.21
1179.73	1155.47	1008.4	1002.94	992.703
968.601	954.993	888.47	879.7	816.856
774.159	725.492	673.657	574.5	528.934
484.028	446.644	443.058	351.422	307.739
233.412	195.474	100.907		

***p* 1**

3238.33	3190.46	3187.91	3161.53	3159.66
3152.33	2726.91	1727	1665.89	1654.57
1467.13	1409.44	1383.04	1328.41	1232.1
1213.27	1142.93	1096.39	1092.15	1034.55
1004.57	984.872	963.839	935.91	920.408
837.852	804.188	786.985	780.737	697.648
685.097	590.908	479.534	440.113	423.118
365.667	297.015	226.869	78.6873	

***p* 2**

3253.67	3195	3168.57	3159.47	3155.89
3012.56	2996.69	1766.06	1662.87	1512.07
1465.29	1440.86	1405.89	1355.32	1324.23
1278.51	1237.48	1169.69	1164.18	1070.77
1023.84	943.816	930.486	926.918	841.758
783.863	782.959	742.566	712.075	609.942
590.139	545.4	493.286	456.702	436.407
338.25	277.94	172.524	42.5276	

***p* 3**

3820.16	3254.27	3199.61	3181.22	3174.68
3158.09	3150.67	1619.07	1581.78	1514.98
1495.56	1464.85	1365.19	1328.02	1312.83
1289.86	1188.11	1175.47	1133.56	1005.88
974.841	949.539	914.886	849.132	839.066
810.501	775.163	735.68	681.628	646.128
513.736	508.693	467.344	423.977	396.142
377.755	332.257	318.735	141.276	

***p* -QM**

3243.71	3199.19	3197.18	3164.38	3162.19
3154.21	1732.63	1699.09	1634.63	1631.85
1463.06	1432.18	1374.42	1351.32	1257.45
1183.72	1119.04	1019.48	992.647	973.323
959.502	954.917	893.356	825.367	797.179
785.174	772.174	682.771	609.398	505.77
460.521	453.393	357.683	343.726	262.426
104.981				

TS*p* 1

3248.48	3203.23	3197.48	3171.25	3163.08
3157	1883.24	1659.99	1565.48	1538.35
1478.76	1425.22	1403.94	1345.26	1305.83
1204.85	1173.03	1083.16	1022.41	992.57
965.945	949.014	911.409	876.507	851.962
815.16	792.039	759.41	730.438	640.929
603.873	496.442	450.032	435.513	371.47
330.71	299.546	118.324		

TS*p* 2

3244.48	3203.57	3199.35	3168.86	3164.79
3155.16	1738.91	1679.73	1625.56	1590.2
1461.06	1430.05	1372.3	1349.02	1252.34
1180.04	1115.3	1015.63	993.421	972.672
957.636	950.137	888.999	832.239	797.068
784.647	768.579	678.313	608.752	518.742
460.113	453.958	378.081	343.617	297.742
261.699	195.953	104.453		

TS*p* 3

3245.37	3196.92	3194.89	3169.58	3168.14
3155.04	2335.08	1634.87	1575.95	1567.76
1471.47	1447.27	1369.74	1336.85	1263.69
1222.55	1162.18	1124.3	991.858	972.67
968.365	967.251	878.011	845.834	827.563
805.757	752.287	734.913	718.642	643.258
616.068	491.188	452.356	419.651	372.991
323.506	284.271	114.025		

TS*p* 4

3244.1	3200.21	3198.3	3167.93	3166.08
3154.67	1672.87	1641.86	1610.89	1582.14
1458.72	1440.48	1372.27	1351.04	1265.18
1179.18	1122.71	1013.51	987.411	973.923
963.448	944.895	889.971	823.648	804.716
786.449	777.093	675.084	613.859	521.596
461.534	447.829	364.696	356.109	342.132
251.36	105.221	34.2405		

TS*p* 5

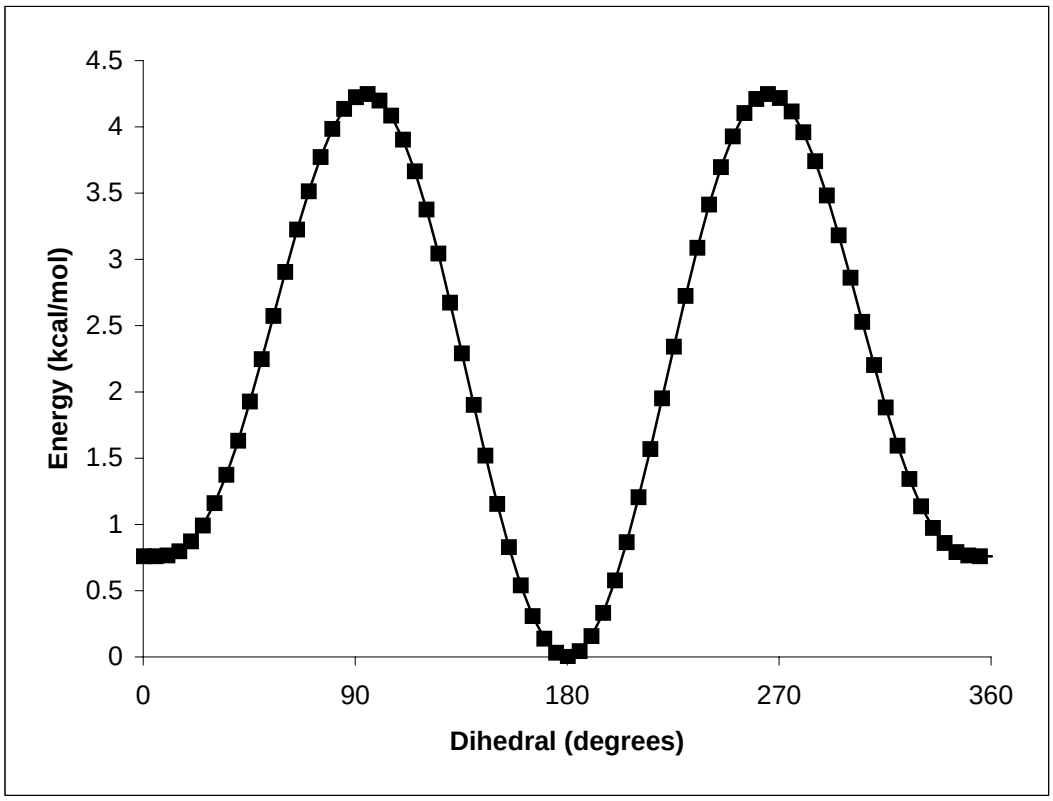
3263.72	3227.7	3225.87	3188.8	3187.15
3171.58	1748.02	1687.75	1667.14	1648.19
1460.39	1436.67	1365.3	1346.25	1246.3
1178.36	1110.98	1034.53	1020.23	974.484
970.759	952.347	883.3	834.739	796.556
793.725	751.795	698.996	602.207	523.67
454.589	446.598	370.17	343.214	274.044
265.291	133.357	98.6727		

NB: M06-2X/6-31G(2df,p) level

Energies (E_0, 0 K + ZPE) and Enthalpies (H_{298}) (hartree)

	G3SX	
	E_0	H_{298}
benzyl	-270.72735455	-270.72073055
***o* 1**	-345.84889523	-345.84113523
***o* 2**	-345.91401327	-345.90599027
***o* 3**	-345.93198137	-345.92428937
***o*-QM**	-345.34330542	-345.33592142
TS*o* 1	-345.83745482	-345.83001182
TS*o* 2	-345.84288660	-345.83438460
TS*o* 3	-345.82721874	-345.81968774
TS*o* 4	-345.83966340	-345.83136140
***p* 1**	-345.85411141	-345.84637441
***p* 2**	-345.90770697	-345.89962197
***p* 3**	-345.93131689	-345.92354689
***p*-QM**	-345.34853212	-345.34116112
TS*p* 1	-345.84022720	-345.83275120
TS*p* 2	-345.84668534	-345.83834634
TS*p* 3	-345.83194284	-345.82437384
TS*p* 4	-345.84155068	-345.83295268
TS*p* 5	-345.83343993	-345.82495393

Internal Rotor Potentials
B3LYP/6-31G(2df,p)



***o* 3**