

Oxidation of the Benzyl Radical: Mechanism, Thermochemistry, and Kinetics for Reactions involving Benzylhydroperoxide

Supporting Information

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Optimized Geometries (B3LYP/6-31G(d), Å)

Benzylperoxy

C	0.35206	1.03099	0.43393
C	1.66879	1.35530	0.11072
C	2.56464	0.35290	-0.26948
C	2.13877	-0.97493	-0.32913
C	0.81938	-1.29799	-0.01049
H	-0.34795	1.80907	0.72357
H	1.99759	2.38980	0.15920
H	3.59220	0.60635	-0.51608
H	2.83197	-1.75831	-0.62311
H	0.48804	-2.33278	-0.05956
C	-0.08373	-0.29997	0.37490
C	-1.50974	-0.64593	0.69657
H	-1.64065	-1.71408	0.88790
H	-1.91025	-0.06293	1.52889
O	-2.40865	-0.39683	-0.44733
O	-2.68036	0.88942	-0.57054

Benzylhydroperoxide

C	-2.58514	-0.25422	0.30595
C	-1.74232	-1.31830	-0.02638
C	-0.42008	-1.07421	-0.39590
C	0.07916	0.23567	-0.43105
C	-0.76865	1.29305	-0.08705
C	-2.09626	1.05226	0.27339
H	-3.61651	-0.44417	0.59076
H	-2.11778	-2.33804	-0.00224
H	0.23719	-1.90023	-0.65678
H	-0.38633	2.31133	-0.09856
H	-2.74427	1.88391	0.53710
C	1.51399	0.48915	-0.84465
H	1.79843	1.53340	-0.66708
H	1.66646	0.26290	-1.90863
O	2.44624	-0.38395	-0.21010
O	2.48840	-0.02072	1.19537
H	1.80150	-0.61217	1.55740

TS1

C	-2.70985	-0.39902	0.18219
C	-1.74245	-1.38381	-0.04102
C	-0.40717	-1.03089	-0.22026
C	-0.02520	0.31761	-0.18310
C	-0.99667	1.30126	0.05062
C	-2.33306	0.94494	0.22650
H	-3.75068	-0.67828	0.32159
H	-2.03197	-2.43081	-0.07648
H	0.35144	-1.78719	-0.39554
H	-0.70466	2.34908	0.08543
H	-3.07951	1.71598	0.39801
C	1.40248	0.72097	-0.35494
H	1.97223	0.62130	0.77678
H	1.58533	1.76822	-0.65100
O	2.28863	-0.14703	-0.81217
O	3.03719	-0.40236	0.90580
H	3.92280	0.01044	0.83227

TS2

C	-2.47533	0.65357	-0.12205
C	-1.32174	1.45572	-0.12110
C	-0.11057	0.82329	0.05885
C	0.06337	-0.55757	0.13092
C	-1.10934	-1.33692	0.12489
C	-2.36192	-0.73121	0.00219
H	-3.45361	1.12213	-0.19568
H	-1.40074	2.53643	-0.20231
H	1.13171	1.39750	0.16859
H	-1.03819	-2.42090	0.16922
H	-3.25533	-1.34968	-0.01550
C	1.44849	-1.16897	0.22866
H	1.42916	-2.28272	0.18056
H	1.77952	-0.99238	1.27625
O	2.36964	-0.72082	-0.64643
O	2.29067	1.35129	0.17121
H	2.72733	2.11847	0.60651

TS3

C	2.33185	-0.48430	-0.01983
C	1.30129	-1.27621	-0.48043
C	-0.00316	-0.73641	-0.58619
C	-0.22594	0.61793	-0.21310
C	0.84353	1.42911	0.19582
C	2.10562	0.87500	0.31997
H	3.33694	-0.88953	0.06139
H	1.48374	-2.30214	-0.78475
H	-0.76492	-1.24669	-1.15879
H	0.66081	2.46162	0.48382
H	2.92799	1.47486	0.69978
C	-1.66101	1.04473	-0.17482
H	-1.77219	1.70908	-1.07550
H	-1.84184	1.71997	0.68855
O	-2.52202	0.03346	-0.31443
O	-1.22765	-1.33268	1.05913
H	-2.18637	-1.35249	0.87939

TS4

C	2.60603	0.60439	0.08332
C	1.52505	1.42997	-0.24519
C	0.24578	0.89886	-0.36174
C	0.03501	-0.47659	-0.12626
C	1.12673	-1.29896	0.22374
C	2.40411	-0.76083	0.31754
H	3.60474	1.02475	0.16454
H	1.68459	2.49210	-0.40854
H	-0.61192	1.52350	-0.58619
H	0.96193	-2.35644	0.41720
H	3.24348	-1.39791	0.58181
C	-1.28397	-1.03622	-0.23986
H	-1.50874	-1.98629	0.25369
H	-2.19278	-1.05623	-1.36510
O	-2.34030	-0.25423	-0.58012
O	-2.82876	0.86877	0.86011
H	-3.78129	0.67657	0.79333

Vibrational Frequencies (B3LYP/6-31G(d), cm⁻¹)

Benzylperoxy

3215.6	3208.3	3198.9	3188.4	3180.6
3156.6	3095.1	1665.1	1646.0	1547.2
1505.5	1503.2	1379.9	1369.2	1361.4
1278.9	1237.3	1215.6	1194.8	1171.1
1122.0	1058.5	1019.6	1005.6	999.9
969.5	935.2	859.7	856.0	829.9
764.5	712.1	635.7	612.0	512.9
473.1	416.7	319.3	297.0	142.5
89.7	38.3			

Benzylhydroperoxide

3670.6	3210.7	3200.6	3192.6	3183.7
3178.8	3091.5	3043.8	1665.7	1645.9
1546.0	1505.2	1493.5	1404.6	1397.5
1366.0	1346.8	1284.0	1228.4	1210.9
1193.4	1120.2	1060.1	1049.2	1018.5
1011.3	998.5	971.7	925.2	884.2
865.7	825.9	756.4	714.0	634.6
631.8	485.3	456.4	416.8	379.9
284.1	232.7	198.4	89.5	36.4

TS1

3669.4	3220.0	3208.7	3195.9	3185.9
3172.4	2999.0	1732.2	1656.2	1639.2
1540.7	1503.5	1409.2	1367.3	1334.5
1306.3	1259.5	1214.3	1200.1	1192.3
1109.9	1054.3	1016.0	998.5	970.1
969.3	919.0	859.5	836.3	799.7
750.2	707.6	632.5	627.8	580.8
508.5	484.3	414.7	399.4	342.7
246.5	199.3	97.8	58.9	

TS2

3576.0	3207.9	3198.3	3187.1	3179.6
2876.9	2868.1	1621.7	1586.1	1543.3
1478.4	1455.5	1368.1	1336.6	1315.3
1234.5	1208.7	1187.9	1152.9	1126.9
1108.3	1053.4	1012.8	973.8	945.6
924.9	864.2	805.0	775.7	757.4
720.0	682.6	647.3	576.1	494.7
411.4	399.1	343.0	277.2	240.2
205.5	168.8	141.5	104.4	

TS3

3715.3	3257.3	3217.4	3208.5	3194.5
3185.6	2902.7	2782.5	1637.2	1588.5
1518.7	1473.2	1411.8	1382.5	1355.1
1307.5	1243.6	1205.2	1195.6	1174.5
1094.3	1060.2	1033.4	1005.7	995.5
962.4	932.5	872.7	839.5	795.2
747.4	712.8	650.9	616.3	604.8
458.2	436.5	418.1	383.1	311.3
259.4	225.2	156.9	105.4	

TS4

3719.6	3237.5	3213.4	3203.2	3191.9
3182.4	3115.3	2268.5	1654.3	1627.6
1541.2	1506.8	1444.2	1374.8	1353.8
1286.3	1227.2	1207.2	1194.7	1115.1
1051.6	1013.3	1004.2	976.5	944.6
912.8	856.1	843.0	801.7	773.1
696.7	632.2	627.8	593.2	496.8
443.0	424.4	411.4	345.3	229.1
181.6	121.6	87.1	59.6	

Rate constants for the benzylperoxy + H association reaction ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)

		C ₆ H ₅ CH ₂ OO—H Distance (Å)						
		2.0	2.1	2.2	2.3	2.5	2.8	3
Temperature (K)	300	1.40×10 ¹⁶	1.50×10 ¹⁵	3.20×10 ¹⁴	1.09×10 ¹⁴	2.95×10 ¹³	1.62×10 ¹³	1.39×10¹³
	400	1.86×10 ¹⁵	3.88×10 ¹⁴	1.31×10 ¹⁴	6.27×10 ¹³	2.59×10 ¹³	1.94×10 ¹³	1.86×10¹³
	500	5.94×10 ¹⁴	1.85×10 ¹⁴	8.29×10 ¹³	4.85×10 ¹³	2.59×10 ¹³	2.35×10¹³	2.39×10 ¹³
	600	2.91×10 ¹⁴	1.19×10 ¹⁴	6.43×10 ¹³	4.30×10 ¹³	2.73×10¹³	2.81×10 ¹³	2.99×10 ¹³
	700	1.81×10 ¹⁴	8.96×10 ¹³	5.57×10 ¹³	4.11×10 ¹³	2.96×10¹³	3.33×10 ¹³	3.65×10 ¹³
	800	1.30×10 ¹⁴	7.48×10 ¹³	5.15×10 ¹³	4.09×10 ¹³	3.23×10¹³	3.89×10 ¹³	4.36×10 ¹³
	900	1.03×10 ¹⁴	6.65×10 ¹³	4.96×10 ¹³	4.17×10 ¹³	3.54×10¹³	4.50×10 ¹³	5.13×10 ¹³
	1000	8.73×10 ¹³	6.16×10 ¹³	4.90×10 ¹³	4.31×10 ¹³	3.88×10¹³	5.15×10 ¹³	5.95×10 ¹³
	1100	7.72×10 ¹³	5.87×10 ¹³	4.92×10 ¹³	4.49×10 ¹³	4.24×10¹³	5.83×10 ¹³	6.81×10 ¹³
	1200	7.04×10 ¹³	5.70×10 ¹³	4.99×10 ¹³	4.71×10 ¹³	4.62×10¹³	6.54×10 ¹³	7.72×10 ¹³
	1300	6.58×10 ¹³	5.62×10 ¹³	5.10×10 ¹³	4.94×10¹³	5.01×10 ¹³	7.27×10 ¹³	8.66×10 ¹³
	1400	6.25×10 ¹³	5.59×10 ¹³	5.24×10 ¹³	5.19×10¹³	5.42×10 ¹³	8.04×10 ¹³	9.63×10 ¹³
	1500	6.02×10 ¹³	5.60×10 ¹³	5.40×10¹³	5.46×10 ¹³	5.84×10 ¹³	8.82×10 ¹³	1.06×10 ¹⁴
	1600	5.86×10 ¹³	5.65×10 ¹³	5.58×10¹³	5.74×10 ¹³	6.27×10 ¹³	9.62×10 ¹³	1.17×10 ¹⁴
	1700	5.75×10 ¹³	5.71×10¹³	5.77×10 ¹³	6.02×10 ¹³	6.71×10 ¹³	1.04×10 ¹⁴	1.27×10 ¹⁴
	1800	5.68×10¹³	5.80×10 ¹³	5.97×10 ¹³	6.31×10 ¹³	7.16×10 ¹³	1.13×10 ¹⁴	1.38×10 ¹⁴
	1900	5.64×10¹³	5.90×10 ¹³	6.17×10 ¹³	6.61×10 ¹³	7.62×10 ¹³	1.21×10 ¹⁴	1.49×10 ¹⁴
	2000	5.62×10¹³	6.01×10 ¹³	6.39×10 ¹³	6.92×10 ¹³	8.08×10 ¹³	1.30×10 ¹⁴	1.60×10 ¹⁴

^a Values in bold indicate the minimum rate constant at each temperature. Non-contributing transition state structures omitted.