ELECTRONIC SUPPLEMENTARY INFORMATION

Role of Conformational Structures and Torsional Anharmonicity in Controlling Chemical Reaction Rates and Relative Yields: Butanal + HO_2 Reactions

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Table of Contents

Cartesian coordinates

M08-HX/maug-cc-pVTZ optimized Cartesian coordinates (in Å) and unscaled frequencies of all the structures of butanal (reactant), butanoyl radical, 1-oxo-2-butyl radical, 4-oxo-2-butyl radical (product radicals), and six lowest-energy structures of the transition states leading to the formation of butanoyl radical, 1-oxo-2-butyl radical, 4-oxo-2-butyl radical, and 4-oxo-1-butyl radical. The structure numbering is the same as in Tables S5 and S6. To obtain scaled frequencies, the unscaled frequencies are to be multiplied by 0.976 (the scaling factor).

A. butanal

Structure 1: zero-point-exclusive relative conformational energy = 0.0 kcal/mol

C	1.39357031	0.12478918	-0.23611705
O	1.45875262	-0.95982328	0.27099676
H	2.26038275	0.52672536	-0.80674530
C	0.19914905	1.03811590	-0.14593793
H	0.54300736	1.93914441	0.38093352
H	-0.03997655	1.37456721	-1.16441697
C	-1.00868205	0.40630046	0.53303188
H	-1.73187617	1.19011046	0.77816741
H	-0.68669363	-0.04106339	1.47874360
C	-1.66808590	-0.65681858	-0.34063844
H	-2.53620795	-1.09615179	0.15627200
H	-0.96594863	-1.46347101	-0.56509967
H	-2.00841660	-0.22559674	-1.28785946

Unscaled frequencies:

123.1	166.2	203.2	282.9	360.9	657.8	705.5	795.2
858.1	948.3	964.9	1057.0	1122.6	1149.8	1249.7	1292.6
1361.7	1383.9	1402.3	1413.5	1437.1	1474.0	1488.8	1498.7
1859.4	2920.5	3022.4	3040.8	3050.9	3061.7	3095.8	3119.6
3135.4							

Structure 3: zero-point-exclusive relative conformational energy = 0.09 kcal/mol

C	-1.55821503	0.40399262	-0.00000271
O	-1.98827964	-0.71523339	-0.00000342
H	-2.25594577	1.27102548	-0.00000907
C	-0.09412757	0.74738134	0.00000503
H	0.09217101	1.39169462	-0.87135178
H	0.09216152	1.39169524	0.87136321
C	0.82201034	-0.46575617	0.00000869
H	0.59174678	-1.08549374	-0.87231170
H	0.59176245	-1.08547817	0.87234453
C	2.29258419	-0.06631806	-0.00000679
H	2.53785440	0.53254342	0.88286235
H	2.53783951	0.53252716	-0.88289111
H	2.94513562	-0.94244529	-0.00000435

Unscaled frequencies

87.0 175.1 195.2 242.7 343.8 664.7 700.3 784.8
866.7 946.5 966.1 1064.1 1140.5 1157.8 1250.1 1307.5
1318.0 1396.7 1406.0 1412.2 1443.1 1480.5 1490.2 1498.0
1860.1 2919.9 3016.8 3036.2 3048.5 3057.9 3091.9 3115.0
3126.0

Structure 4: zero-point-exclusive relative conformational energy = 1.04 kcal/mol

C	1.18543414	0.06249244	0.37143889
O	2.04408706	-0.58163365	-0.16021938
H	1.10986811	0.08473534	1.48507040
C	0.14089609	0.87719017	-0.34352214
H	0.38052618	1.93439533	-0.17036215
H	0.21631539	0.68130612	-1.41692296
C	-1.25625737	0.56204612	0.19711471
H	-1.97933869	1.25129167	-0.24817428
H	-1.27483211	0.75178655	1.27741910
C	-1.65880123	-0.88175193	-0.08510464
H	-0.95694927	-1.58578527	0.37435166
H	-1.66014804	-1.08042971	-1.16102438
H	-2.65576786	-1.10409168	0.30183679

Unscaled frequencies:

59.8 117.7 220.3 297.1 398.0 517.7 752.2 782.7
906.8 947.3 979.2 1071.4 1130.3 1162.8 1234.9 1274.7
1342.9 1365.8 1408.9 1414.9 1450.3 1480.3 1490.6 1492.8
1866.3 2891.5 3035.2 3037.9 3040.0 3088.0 3108.7 3115.0
3130.0

Structure 6: zero-point-exclusive relative conformational energy = 1.20 kcal/mol

C	1.44936594	0.22938842	0.27150973
O	2.41910683	-0.12322110	-0.33756328
H	1.49265756	1.14094961	0.91264836
C	0.11370496	-0.45998057	0.24080052
H	0.16811092	-1.31027042	-0.44448026
H	-0.08317500	-0.84731310	1.25033522
C	-1.00779282	0.50756508	-0.14622706
H	-0.82802846	0.88181304	-1.15994309
H	-0.97817546	1.38055335	0.51684547
C	-2.37799658	-0.15515047	-0.07046758
H	-2.58460795	-0.50676775	0.94496778
H	-2.42936141	-1.02060655	-0.73758048
H	-3.17396385	0.53647591	-0.35598042

Unscaled frequencies:

67.4 96.9 228.3 251.1 382.2 514.1 739.5 802.7
907.5 951.4 1020.6 1065.9 1144.1 1166.2 1248.5 1279.2
1321.0 1376.2 1404.4 1417.1 1454.7 1483.0 1488.8 1497.7
1865.5 2901.6 3023.7 3036.0 3041.1 3075.3 3110.5 3118.4
3128.4

B. butanoyl radical

Structure 1: zero-point-exclusive relative conformational energy = 0.0 kcal/mol

C	-1.42610573	0.17001580	-0.29163774
O	-1.59643822	-0.86975010	0.22414157
C	-0.19960915	1.06149054	-0.21028510
H	0.05615691	1.34753731	-1.23612620
H	-0.54337675	1.97841147	0.28088167
C	0.97851352	0.41462001	0.51681499
H	0.63751727	0.05532780	1.49303713
H	1.73346196	1.18506186	0.70556936
C	1.58895186	-0.73355803	-0.27887790
H	1.94712899	-0.38506052	-1.25271117
H	0.85370479	-1.52396917	-0.45055600
H	2.43640960	-1.17471789	0.25068716

Unscaled frequencies:

107.9	162.8	199.6	274.1	352.8	627.6	768.5	795.4
841.1	910.7	1048.4	1065.7	1115.3	1227.7	1272.1	1328.1
1362.8	1405.1	1432.0	1472.6	1489.5	1497.1	1979.5	3042.8
3049.2	3056.8	3090.5	3101.7	3122.5	3134.0		

Structure 3: zero-point-exclusive relative conformational energy = 0.11 kcal/mol

C	-1.59859163	0.46884933	-0.00001237
O	-2.10985157	-0.58672318	-0.00008009
C	-0.11455605	0.77665790	0.00003926
H	0.07309376	1.41218406	-0.87291565
H	0.07305234	1.41208900	0.87307232
C	0.76727295	-0.46906526	-0.00000754
H	0.52176299	-1.07866753	-0.87516606
H	0.52172252	-1.07876196	0.87507387
C	2.24633654	-0.10268687	0.00004643
H	2.50456972	0.48950670	0.88336010
H	2.50461058	0.48960145	-0.88319179
H	2.87722970	-0.99469690	0.00001322

Unscaled frequencies:

75.8	160.7	184.1	238.3	335.3	646.6	705.0	831.7
843.3	927.0	1057.5	1067.2	1120.9	1238.3	1269.6	1313.9
1364.7	1404.2	1436.5	1480.9	1488.9	1496.3	1981.3	3038.3
3049.1	3060.0	3083.5	3100.9	3119.2	3126.4		

Structure 4: zero-point-exclusive relative conformational energy = 0.28 kcal/mol

C	1.18871441	-0.09411941	-0.37347391
O	2.20986126	-0.47134156	0.05830992
C	0.16600175	0.82003833	0.28202621
H	0.23834308	0.68063076	1.36813382
H	0.50880817	1.83493943	0.04896831
C	-1.24504326	0.57269990	-0.23627588
H	-1.25542227	0.72007138	-1.32111500
H	-1.91743352	1.32119045	0.19363892
C	-1.72832276	-0.83185565	0.10483423
H	-1.73603470	-0.99001602	1.18787244
H	-1.06696428	-1.58463425	-0.33697289
H	-2.73828743	-1.01202827	-0.26966886

Unscaled frequencies:

49.6	153.3	220.5	294.8	380.2	513.9	752.5	779.9
874.8	915.7	1036.8	1061.5	1120.4	1218.2	1269.3	1327.6
1370.4	1404.7	1427.3	1475.6	1488.9	1493.5	1989.9	3027.7
3035.1	3052.9	3089.1	3094.1	3114.7	3130.0		

Structure 6: zero-point-exclusive relative conformational energy = 0.71 kcal/mol

C	1.48617043	0.29257285	0.21125179
O	2.53144407	-0.07149173	-0.17178992
C	0.14659504	-0.41191534	0.10712524
H	0.19443048	-1.12215161	-0.72794187
H	0.05808789	-0.99369568	1.03365724
C	-1.02688896	0.55194898	-0.02371074
H	-0.90408458	1.15013687	-0.93258854
H	-1.00458418	1.25505912	0.81484147
C	-2.35604214	-0.19186543	-0.06159371
H	-2.50421531	-0.77425813	0.85305734
H	-2.39382870	-0.88664233	-0.90607244
H	-3.19636440	0.49903923	-0.15906929

Unscaled frequencies:

50.9	108.5	223.9	244.3	397.6	479.9	722.3	815.8
884.2	937.8	1048.5	1065.9	1129.4	1234.0	1259.2	1318.1
1372.5	1406.3	1433.0	1483.1	1489.2	1498.3	1989.7	3022.9
3039.8	3051.8	3075.4	3095.2	3118.1	3130.3		

C. 1-oxo-2-butyl radical

Structure 1: zero-point-exclusive relative conformational energy = 0.0 kcal/mol

C	-1.50045194	0.41547185	-0.11272504
O	-1.92893916	-0.73016223	-0.13500438
C	-0.13628668	0.73828410	0.17132814
H	0.15498963	1.78521851	0.16225036
C	0.88168418	-0.29425739	0.47317989
H	0.44100533	-1.28167892	0.31273234
H	1.13714157	-0.23148515	1.54129662
C	2.15909973	-0.11029244	-0.35313847
H	2.59721697	0.87799999	-0.18636091
H	1.94958382	-0.20984756	-1.42093004
H	2.90546198	-0.86029974	-0.08281564
H	-2.17815771	1.26615397	-0.31800482

Unscaled frequencies:

34.6	205.4	222.8	287.3	387.7	655.2	706.1	786.8
886.5	972.5	1018.0	1057.3	1079.4	1189.5	1266.6	1314.6
1395.3	1406.3	1456.7	1467.8	1488.8	1494.9	1643.4	2973.9
3006.5	3045.8	3101.8	3126.8	3135.5	3181.1		

Structure 3: zero-point-exclusive relative conformational energy = 0.76 kcal/mol

C	1.37532211	0.28525216	-0.19335162
O	2.44412690	-0.29854441	-0.08682536
C	0.15861625	-0.17769151	0.38999098
H	0.20520950	-1.10936993	0.94789613
C	-1.13265678	0.53758207	0.26129132
H	-1.00289164	1.42491948	-0.36785532
H	-1.44147032	0.89936715	1.25261244
C	-2.24325519	-0.36040634	-0.29934481
H	-2.38628392	-1.24070100	0.33298987
H	-1.99422112	-0.70665348	-1.30519823
H	-3.19092077	0.18021103	-0.34791772
H	1.30940474	1.23216370	-0.76943955

Unscaled frequencies:

65.5	167.8	206.0	297.5	384.5	546.1	735.6	775.2
923.3	959.5	1015.1	1059.5	1169.3	1192.9	1263.4	1299.6
1376.7	1397.5	1453.3	1468.6	1487.7	1496.6	1637.5	2943.1
3008.1	3048.7	3074.6	3129.9	3137.0	3179.6		

Structure 5: zero-point-exclusive relative conformational energy = 1.32 kcal/mol

C	-1.11448370	-0.34689917	-0.00004352
O	-2.33309858	-0.21118262	-0.00008401
C	-0.21690558	0.75930356	0.00000205
H	-0.68333094	1.74040673	-0.00000141
C	1.26513318	0.67437640	0.00005153
H	1.64007195	1.23679413	0.86769714
H	1.64013080	1.23681216	-0.86755702
C	1.85235297	-0.73351261	0.00005668
H	1.54091576	-1.29659652	-0.88380721
H	1.54085293	-1.29661620	0.88388591
H	2.94315165	-0.68935771	0.00009588
H	-0.67358477	-1.36159066	-0.00004166

Unscaled frequencies:

128.5	173.5	223.5	292.7	416.6	592.6	698.8	787.1
907.2	955.6	1003.2	1065.9	1121.6	1205.4	1270.6	1342.9
1376.4	1412.1	1442.1	1470.5	1491.8	1497.1	1619.1	2984.2
3002.7	3025.2	3049.7	3125.5	3136.3	3185.1		

Structure 6: zero-point-exclusive relative conformational energy = 1.92 kcal/mol

C	1.40683446	0.23339313	-0.00007198
O	1.40131292	-0.99039994	-0.00017417
C	0.24430441	1.06514398	0.00007841
H	0.43240865	2.13551648	0.00015840
C	-1.17797195	0.63869391	0.00014068
H	-1.66084430	1.11766887	-0.86557821
H	-1.66071518	1.11749157	0.86603007
C	-1.47751414	-0.85678069	0.00001032
H	-1.05397650	-1.34828116	0.87694433
H	-1.05409512	-1.34810367	-0.87708061
H	-2.55915832	-1.01222439	0.00006750
H	2.37196086	0.77842995	-0.00009272

Unscaled frequencies:

29.1	231.4	245.1	315.5	366.2	647.6	757.1	787.0
833.3	969.6	998.8	1061.4	1088.2	1178.3	1272.3	1371.8
1411.8	1414.9	1433.0	1471.3	1484.5	1488.2	1639.9	2955.9
2991.9	3012.2	3060.1	3139.4	3151.9	3177.0		

D. 4-oxo-2-butyl radical

Structure 1: zero-point-exclusive relative conformational energy = 0.0 kcal/mol

C	1.54733488	0.37120726	-0.00000067
O	1.95502589	-0.75497541	-0.00000578
C	0.08924240	0.75322570	0.00000276
H	-0.06636575	1.42084264	0.86655638
H	-0.06636796	1.42084966	-0.86654505
C	-0.85216409	-0.38855027	-0.00000063
H	-0.44283866	-1.38879009	-0.00000581
C	-2.31493294	-0.14368399	0.00000215
H	-2.62833923	0.44091398	-0.87752882
H	-2.62833665	0.44090916	0.87753723
H	-2.88521248	-1.07389206	0.00000037
H	2.25872182	1.22608493	0.00000190

Unscaled frequencies:

55.2	75.0	161.3	201.2	311.5	348.7	685.0	703.3
867.0	969.8	971.1	1020.2	1123.9	1169.2	1203.8	1290.4
1394.7	1409.6	1416.6	1442.3	1462.0	1476.5	1862.9	2925.6
2961.1	2972.7	2987.2	3026.6	3131.6	3239.6		

Structure 2: zero-point-exclusive relative conformational energy = 0.32 kcal/mol

C	1.39984524	0.09404373	0.16431531
O	1.37158687	-1.03586209	-0.22960853
C	0.22384857	1.05565790	0.12879985
H	0.07409396	1.36824304	1.17602426
H	0.56761478	1.95497895	-0.39738525
C	-1.02015148	0.49546991	-0.45294816
H	-1.26036520	0.71726529	-1.48419224
C	-1.75017896	-0.58353901	0.25666251
H	-1.80315967	-0.38454397	1.33406076
H	-1.23439817	-1.54886165	0.14122262
H	-2.76841661	-0.70469348	-0.11978739
H	2.33175563	0.51471335	0.60594840

Unscaled frequencies:

74.2	141.6	144.6	217.6	362.6	417.4	690.7	737.2
845.0	943.4	973.0	994.0	1130.7	1163.5	1244.9	1309.9
1369.2	1400.4	1410.1	1440.9	1464.2	1478.8	1858.6	2911.3
2985.9	2993.4	3055.6	3063.6	3120.2	3221.4		

Structure 4: zero-point-exclusive relative conformational energy = 0.37 kcal/mol

C	1.26123461	0.18276284	-0.29038570
O	1.66758607	-0.88355273	0.07821829
C	0.16686103	0.95667705	0.42303648
H	0.16336531	0.64418836	1.47338486
H	0.36039669	2.03026293	0.35073805
C	-1.10769664	0.57940519	-0.25581735
H	-1.50304979	1.21366753	-1.03742675
C	-1.71591049	-0.74259232	0.03231808
H	-2.08700536	-0.78970499	1.06620536
H	-0.97271795	-1.54825419	-0.05502741
H	-2.54902468	-0.96769156	-0.63510536
H	1.62041612	0.62843726	-1.24342411

Unscaled frequencies:

76.1	95.5	122.1	247.4	367.6	410.3	506.3	850.2
914.0	952.1	979.5	1026.8	1130.4	1146.4	1225.3	1259.2
1367.9	1400.6	1417.8	1450.4	1458.1	1476.2	1841.9	2930.7
2994.0	3038.2	3041.2	3116.0	3135.2	3227.7		

Structure 6: zero-point-exclusive relative conformational energy = 1.13 kcal/mol

C	1.42190041	0.32349470	0.10963827
O	2.41144737	-0.20399807	-0.30767529
C	0.10659648	-0.38058971	0.33696101
H	0.11690427	-1.33495464	-0.20240898
H	0.08031395	-0.64302905	1.41290023
C	-1.06077914	0.46317786	-0.02897916
H	-0.94949133	1.54095607	-0.00386964
C	-2.40877625	-0.13936350	-0.16945239
H	-2.81475472	-0.46194692	0.80245463
H	-2.37805535	-1.03656368	-0.79965575
H	-3.12561651	0.55939101	-0.60483389
H	1.42547167	1.40781571	0.36780938

Unscaled frequencies:

46.8	88.3	117.3	219.9	362.5	395.8	514.0	725.9
934.3	960.8	1026.0	1032.2	1133.8	1170.9	1192.7	1267.0
1389.1	1414.1	1425.0	1430.9	1464.2	1476.2	1870.4	2909.5
2927.2	2981.0	3051.0	3063.7	3128.1	3199.9		

E. transition states leading to the formation of butanoyl radical

Structure 1: zero-point-exclusive relative conformational energy = 0.0 kcal/mol

C	0.04052814	1.12909383	0.08884913
O	-0.39586432	1.96868831	-0.61427943
H	-0.78888230	0.30201845	0.64360163
O	-1.67339569	-0.56854665	0.88096155
O	-2.23928206	-0.76453169	-0.36357894
H	-2.95321024	-0.11872905	-0.39737824
C	1.48635812	0.80487298	0.39124294
H	2.10433223	1.26171833	-0.38898916
H	1.71604027	1.29751202	1.34375318
C	1.68498653	-0.70693231	0.48799237
H	1.07920080	-1.09524538	1.31377957
H	2.73098383	-0.90891477	0.73566392
C	1.29150919	-1.40536865	-0.80907904
H	1.86890572	-1.01724807	-1.65424668
H	0.22778457	-1.25403012	-1.02699247
H	1.46288987	-2.48195617	-0.74804953

Unscaled frequencies:

-1803.9	50.1	54.1	91.7	115.7	152.1	227.6	296.7
356.0	386.3	424.6	479.3	594.0	766.6	829.9	904.8
951.7	1033.3	1066.2	1074.1	1136.5	1170.2	1231.6	1273.3
1332.5	1369.4	1412.4	1421.7	1433.5	1463.8	1480.0	1489.8
1495.6	1941.1	3033.5	3042.0	3054.3	3091.9	3102.4	3115.1
3132.5	3835.7						

Structure 3: zero-point-exclusive relative conformational energy = 0.32 kcal/mol

C	0.18653748	1.21654408	0.01780036
O	0.22942480	2.05939234	-0.80536495
H	-0.94491785	0.71953769	0.38087061
O	-1.99028422	0.04485228	0.67500517
O	-2.03405190	-0.92522523	-0.30973509
H	-2.62193990	-0.54854280	-0.97311649
C	1.33011809	0.54350427	0.74081434
H	2.26944746	0.92038826	0.32333085
H	1.25622077	0.85314668	1.78954340
C	1.20885172	-0.97855587	0.62188966
H	0.25406769	-1.29576291	1.05415787
H	2.00126310	-1.43353813	1.22318883
C	1.30373352	-1.44234023	-0.82658537
H	2.24278271	-1.11683619	-1.28520774
H	0.47732827	-1.03479823	-1.41854697
H	1.24959346	-2.53066303	-0.89697533

Unscaled frequencies:

-1730.9	53.0	58.9	104.6	111.2	133.7	202.8	295.5
362.7	387.0	431.0	512.7	580.9	776.6	836.3	903.8
941.5	1052.0	1067.4	1077.6	1145.4	1208.4	1258.1	1288.5
1331.4	1347.0	1369.2	1409.2	1415.0	1441.5	1477.3	1489.1
1491.5	1941.4	3036.4	3044.1	3059.2	3095.5	3107.6	3118.6
3132.2	3835.5						

Structure 5: zero-point-exclusive relative conformational energy = 0.33 kcal/mol

C	0.18238996	0.00934970	-0.10004025
O	0.16292190	-1.14356254	-0.35357125
H	1.34238428	0.50502609	0.26744888
O	2.53839486	0.66681824	0.52857681
O	3.13472318	-0.32309759	-0.22555730
H	3.15685547	-1.08327448	0.36547102
C	-0.96130302	0.99189798	-0.18204218
H	-0.98367544	1.53879883	0.76838735
H	-0.65797439	1.72599174	-0.93854043
C	-2.30220582	0.33884982	-0.50219286
H	-2.18940481	-0.28151444	-1.39690032
H	-3.01943054	1.12790123	-0.74905143
C	-2.82716123	-0.50309831	0.65558067
H	-2.95715597	0.10814617	1.55420440
H	-2.13604244	-1.31580660	0.89354932
H	-3.79419502	-0.94852850	0.41201293

Unscaled frequencies:

-1962.3	35.9	56.0	64.5	128.9	178.7	205.8	255.7
293.7	369.9	400.7	452.1	684.3	777.0	816.8	879.8
955.0	1014.9	1053.8	1075.3	1120.4	1137.7	1240.5	1283.6
1346.8	1367.0	1405.8	1425.3	1431.0	1473.6	1489.5	1497.6
1528.9	1930.3	3043.6	3045.0	3053.6	3085.0	3097.2	3123.6
3135.1	3839.1						

Structure 7: zero-point-exclusive relative conformational energy = 0.34 kcal/mol

C	-0.18231927	0.13857611	-0.31688160
O	-0.16379004	-0.92602143	-0.82688171
H	-1.36463849	0.60196046	0.02014881
O	-2.57132110	0.73150783	0.24895009
O	-2.98333639	-0.57930286	0.37655656
H	-3.23009026	-0.83304416	-0.51921281

C	0.99261938	1.03745089	-0.01377238
H	0.82892879	1.94401734	-0.60935868
H	0.89292020	1.34888392	1.03302071
C	2.34358457	0.38697649	-0.29525246
H	3.11483829	1.16246671	-0.25282073
H	2.34196794	-0.00624332	-1.31683109
C	2.66567599	-0.72767101	0.69413434
H	1.91898182	-1.52422856	0.64373691
H	2.68576027	-0.34449563	1.71912227
H	3.64154766	-1.17077992	0.48382768

Unscaled frequencies:

-1962.2 35.2 60.0 64.4 127.0 183.2 206.5 272.8
279.9 366.5 410.0 456.9 681.7 784.0 816.1 877.6
956.4 1013.1 1053.4 1074.9 1115.2 1146.1 1238.7 1282.0
1346.1 1366.8 1407.2 1425.5 1431.4 1473.1 1490.2 1497.2
1528.6 1930.7 3044.1 3045.1 3053.2 3085.0 3096.9 3124.1
3135.6 3840.1

Structure 9: zero-point-exclusive relative conformational energy = 0.42 kcal/mol

C	-0.06588126	1.14112368	0.01928331
O	-0.28498174	2.26102419	-0.27584696
H	0.88137537	0.48463304	-0.53627949
O	1.82361484	-0.34054152	-0.84828883
O	2.23260224	-0.82436125	0.38244402
H	3.00696717	-0.29073121	0.58918378
C	-0.77082885	0.27830762	1.04245491
H	-0.07384674	0.16581497	1.88080852
H	-1.65651196	0.82245281	1.38627386
C	-1.11588064	-1.09099143	0.45379610
H	-1.60706772	-1.68356567	1.23101566
H	-0.18863374	-1.61032890	0.19425459
C	-2.01417046	-0.97001815	-0.77179314
H	-1.50826484	-0.42426593	-1.57600391
H	-2.93697763	-0.43135785	-0.53436845
H	-2.28635540	-1.95215292	-1.16379743

Unscaled frequencies:
-1623.1 27.5 71.4 93.4 108.5 165.2 222.4 298.1
352.9 394.3 427.7 481.5 586.8 767.8 826.2 902.7
941.6 1033.0 1065.3 1075.9 1144.6 1155.3 1231.4 1272.4
1335.1 1371.8 1408.3 1410.7 1432.4 1467.1 1481.9 1491.0
1492.9 1942.4 3033.3 3045.6 3065.5 3096.1 3106.5 3121.7
3131.9 3839.6

Structure 11: zero-point-exclusive relative conformational energy = 0.43 kcal/mol

C	0.33424687	0.19953155	-0.13139015
O	0.50563506	1.36746853	-0.13934519
H	1.41310041	-0.54862823	-0.19063442
O	2.57874862	-0.95490480	-0.21273357
O	3.25628267	0.07958618	0.39956838
H	3.49303240	0.66473366	-0.32794952
C	-0.98140682	-0.53154436	-0.04781692
H	-1.02845339	-1.19957252	-0.91720287
H	-0.91555210	-1.19450347	0.82417721
C	-2.18783629	0.39591133	0.02746631
H	-2.19102452	1.04880543	-0.85090296
H	-2.07715343	1.05382828	0.89494247
C	-3.48913200	-0.39200754	0.11449623
H	-3.50338961	-1.03097054	1.00268755
H	-3.61825029	-1.03668250	-0.76024922
H	-4.35287087	0.27444466	0.16868192

Unscaled frequencies:

-1958.9 37.2 57.7 64.6 94.2 157.9 216.5 239.8
285.7 341.2 406.7 446.0 704.8 749.7 823.1 883.4
971.1 1006.4 1060.6 1075.3 1129.6 1148.7 1244.4 1290.8
1315.1 1375.2 1405.2 1425.0 1435.7 1480.6 1489.3 1496.5
1528.2 1932.3 3039.0 3039.9 3059.2 3074.5 3097.8 3119.5
3129.3 3838.2

F. transition states leading to the formation of 1-oxo-2-butyl radical

Structure 1: zero-point-exclusive relative conformational energy = 0.0 kcal/mol

C	-1.32833183	-1.07745471	0.37701740
O	-1.81857138	-0.82696203	-0.70206684
O	-0.37538812	1.60963080	0.77893834
O	-0.37252406	1.78695236	-0.57793846
H	-1.22752162	1.43481626	-0.86696177
C	0.09325674	-0.85938434	0.68278915
H	-0.05994174	0.45893815	0.92873974
H	0.42955662	-1.24268877	1.64672987
C	1.08552352	-0.86930500	-0.44430537
H	0.61522342	-0.43332471	-1.33046107
H	1.30368095	-1.91654226	-0.69898514
C	2.37325668	-0.13081926	-0.09410394
H	2.83701995	-0.54767319	0.80514296
H	2.16501636	0.92703894	0.09027079
H	3.09763153	-0.19803086	-0.90830258
H	-1.97102753	-1.41772272	1.21397947

Unscaled frequencies:

-2101.4	90.8	95.3	131.4	151.8	194.2	221.9	248.1
305.8	389.9	471.2	556.2	692.2	760.2	834.1	881.5
974.3	1011.3	1062.8	1082.9	1095.2	1143.2	1175.4	1272.6
1308.2	1402.5	1406.8	1416.9	1446.1	1459.7	1467.3	1489.8
1493.6	1764.7	2961.4	3011.4	3043.6	3094.0	3122.0	3135.9
3138.5	3763.9						

Structure 3: zero-point-exclusive relative conformational energy = 0.77 kcal/mol

C	-0.06724499	1.33741541	0.47621371
O	0.06273710	1.63033296	-0.69230309
O	2.02151952	-0.60461244	0.56580652
O	1.95623458	-0.67456556	-0.79865826
H	1.96541899	0.24899297	-1.08885626
C	-0.40039276	-0.02122061	0.92828142
H	0.88832786	-0.43701218	0.91532994
H	-0.67151886	-0.10506571	1.98080755
C	-1.08178928	-0.93724515	-0.04778207
H	-1.07752424	-1.95777388	0.34457113
H	-0.51311680	-0.94095514	-0.98296701
C	-2.51970405	-0.48034697	-0.32798203
H	-2.52243289	0.52205086	-0.76377690

H	-3.11389759	-0.45945389	0.58991834
H	-3.00701806	-1.15866579	-1.03206653
H	0.14261843	2.08702702	1.26589220

Unscaled frequencies:

-2131.9	73.2	100.0	106.8	137.0	199.1	222.8	238.4
305.4	393.5	465.9	577.8	668.7	785.9	838.1	880.6
968.5	1005.3	1055.5	1082.7	1098.9	1118.9	1167.9	1283.8
1332.8	1386.3	1403.0	1417.4	1441.6	1466.5	1472.3	1488.0
1495.0	1763.5	2960.1	3044.4	3060.7	3105.1	3127.9	3134.9
3143.5	3776.3						

Structure 5: zero-point-exclusive relative conformational energy = 1.15 kcal/mol

C	0.76768797	1.32055624	0.47110015
O	1.15306889	1.59985335	-0.64242976
O	0.69271317	-1.62124833	0.06616700
O	1.99249064	-1.21605515	-0.07687952
H	2.01293863	-0.77989319	-0.93913983
C	-0.44420220	0.52715374	0.72098445
H	0.13503044	-0.67056958	0.55322345
H	-0.77036710	0.49176185	1.76145295
C	-1.52119812	0.50636602	-0.32914091
H	-1.04626265	0.46370950	-1.31392871
H	-2.06396859	1.46090186	-0.29280103
C	-2.49005282	-0.65622628	-0.13663401
H	-2.96760589	-0.61264737	0.84684226
H	-1.96476407	-1.61282736	-0.21372274
H	-3.27756378	-0.64174329	-0.89291571
H	1.36297241	1.61381031	1.35826955

Unscaled frequencies:

-2074.1	76.5	84.6	89.3	122.6	195.3	204.6	252.3
300.7	352.3	477.9	572.3	694.7	749.5	826.6	879.4
993.7	1009.1	1067.8	1085.9	1116.0	1162.3	1173.4	1271.1
1309.9	1387.6	1404.4	1413.6	1428.2	1452.3	1465.9	1490.7
1494.5	1756.3	2969.7	3021.1	3042.8	3089.3	3119.9	3132.6
3134.2	3801.2						

Structure 7: zero-point-exclusive relative conformational energy = 1.39 kcal/mol

C	0.04616263	1.12348365	0.56932748
O	0.03042451	1.69046590	-0.50026625
O	1.81085117	-1.18994444	-0.04522723

O	2.54195282	-0.03774366	-0.16886061
H	2.28289142	0.31835322	-1.02858469
C	-0.40011847	-0.26897235	0.73814447
H	0.78433912	-0.83475067	0.46634997
H	-0.57368097	-0.57231401	1.77145268
C	-1.32229151	-0.83344731	-0.30798741
H	-1.35004723	-1.92360683	-0.22242655
H	-0.92238290	-0.58996111	-1.29660681
C	-2.73509546	-0.25534340	-0.17066035
H	-2.71624544	0.82933765	-0.30573822
H	-3.15582149	-0.47174645	0.81549799
H	-3.40220814	-0.68064888	-0.92401254
H	0.45538459	1.62879116	1.46595574

Unscaled frequencies:

-2087.0	60.4	69.9	80.9	119.2	198.6	215.6	244.3
298.7	371.4	462.8	613.7	664.8	771.0	821.3	877.8
975.3	998.0	1070.4	1081.7	1098.3	1150.1	1166.6	1281.8
1328.0	1386.7	1395.3	1413.1	1425.3	1445.4	1469.2	1487.1
1494.5	1757.6	2972.2	3043.2	3060.2	3103.3	3126.5	3132.9
3136.7	3805.9						

Structure 9: zero-point-exclusive relative conformational energy = 1.69 kcal/mol

C	0.72849982	-1.29381783	0.25245739
O	1.75565425	-1.52443479	-0.34283643
O	0.72283729	1.63558765	-0.33359543
O	1.79062438	1.35882336	0.47888559
H	2.43956723	0.95556853	-0.11280761
C	-0.42782536	-0.61798135	-0.35251194
H	0.08417557	0.61819851	-0.33418275
H	-0.48644398	-0.74157033	-1.43557539
C	-1.72601239	-0.55888677	0.40205772
H	-1.51859196	-0.40866245	1.46786565
H	-2.23004386	-1.53277493	0.32156721
C	-2.64762067	0.54125952	-0.11806430
H	-2.87506546	0.39012633	-1.17725097
H	-2.17233516	1.52092973	-0.01373013
H	-3.59168654	0.55930612	0.43004652
H	0.63524845	-1.54437254	1.33080444

Unscaled frequencies:

-2069.3	65.7	71.6	84.8	140.9	160.1	202.4	249.9
319.0	392.0	481.0	523.0	540.1	752.1	840.4	923.9

981.8 1039.3 1065.8 1120.3 1130.8 1145.7 1170.1 1262.3
1291.8 1378.6 1404.4 1417.3 1429.2 1451.3 1465.6 1489.6
1495.5 1765.1 2942.8 3009.0 3044.1 3066.0 3120.9 3126.8
3135.8 3802.0

Structure 11: zero-point-exclusive relative conformational energy = 1.85 kcal/mol

C	-0.39785560	1.46155036	0.24952364
O	-0.89760584	1.62926882	-0.83588222
O	1.81835826	-0.57551166	0.61267171
O	2.05885817	0.11335808	-0.55265153
H	1.74439884	-0.48078196	-1.24550943
C	-0.54694167	0.21298869	1.02650530
H	0.71468211	-0.22982961	0.92011587
H	-0.57322276	0.37608629	2.10528470
C	-1.44338397	-0.85913594	0.46354659
H	-2.41054086	-0.39497107	0.22756338
H	-1.63039775	-1.61817450	1.22755360
C	-0.88681051	-1.51471048	-0.80306985
H	0.03869843	-2.05505345	-0.58031888
H	-0.69221213	-0.75950773	-1.56928573
H	-1.60082579	-2.23191179	-1.21331909
H	0.22248568	2.25306612	0.71577784

Unscaled frequencies:

-2176.2 62.9 95.4 109.6 147.7 167.7 201.0 227.7
294.5 392.9 496.7 538.7 574.3 766.2 783.5 926.1
986.0 1039.1 1078.5 1082.1 1137.4 1162.1 1183.3 1262.5
1292.3 1382.3 1407.3 1428.1 1464.2 1468.9 1484.2 1490.3
1493.4 1769.4 2941.4 3005.0 3045.8 3062.5 3116.0 3122.5
3137.0 3743.5

G. transition states leading to the formation of 4-oxo-2-butyl radical

Structure 1: zero-point-exclusive relative conformational energy = 0.0 kcal/mol

C	-1.45000511	-1.11399473	-0.06791535
O	-0.48731352	-1.50437254	-0.66993566
O	1.63782031	-0.21043643	0.97191387
O	2.12205548	-0.40419562	-0.31195101
H	1.52378481	-1.08039668	-0.65945498
C	-1.56927884	0.21419356	0.63386502
H	-2.51134435	0.66712835	0.28008317
H	-1.75212011	-0.01643342	1.69196886

C	-0.41492608	1.16444483	0.46256593
H	0.70219555	0.45409906	0.81654054
H	-0.38528291	1.94456783	1.22386996
C	-0.11362249	1.64087039	-0.92921016
H	-0.91880262	2.29581991	-1.29208552
H	-0.02044253	0.80606517	-1.62769820
H	0.81862706	2.20877250	-0.95791407
H	-2.35011792	-1.76067028	0.00863998

Unscaled frequencies:

-2290.8	87.7	124.6	136.0	168.2	172.4	188.6	223.0
302.4	382.9	506.5	557.8	682.2	719.4	807.5	867.1
959.2	969.1	1051.8	1057.2	1087.0	1142.5	1182.8	1255.9
1346.3	1367.1	1397.0	1414.5	1428.7	1460.2	1467.3	1473.1
1478.1	1852.8	2943.3	2986.0	3008.1	3055.1	3101.3	3122.3
3144.7	3782.1						

Structure 3: zero-point-exclusive relative conformational energy = 0.33 kcal/mol

C	0.42178099	1.83423478	0.15138127
O	1.37616867	1.34349685	-0.38770936
O	0.89160692	-1.37884361	0.76831933
O	1.74007789	-1.50461565	-0.32024188
H	2.06318832	-0.60081058	-0.44186926
C	-0.92208822	1.17270853	0.28699093
H	-1.16282519	1.13999167	1.35964791
H	-1.66542287	1.86797316	-0.13957606
C	-1.02204593	-0.18826545	-0.33886222
H	-0.07157817	-0.91344944	0.30610111
H	-0.57083848	-0.25226702	-1.33161448
C	-2.33002406	-0.90470829	-0.17166247
H	-3.13136374	-0.38413165	-0.71462704
H	-2.62741828	-0.94893564	0.88053018
H	-2.27902026	-1.92487397	-0.55666779
H	0.49671410	2.85238538	0.58804561

Unscaled frequencies:

-2265.6	72.6	119.3	129.4	145.3	182.3	199.5	211.4
226.7	363.0	517.0	563.8	688.1	710.1	849.9	872.3
954.1	972.2	1060.0	1079.0	1116.8	1146.9	1175.3	1243.5
1302.5	1392.4	1406.6	1412.9	1430.7	1463.4=	1473.2	1475.8
1478.7	1851.9	2948.4	2985.9	3009.7	3037.2	3085.5	3110.3
3136.9	3781.4						

Structure 5: zero-point-exclusive relative conformational energy = 0.70 kcal/mol

C	-1.17590596	-1.36036308	0.22881089
O	-1.66613472	-0.98157519	-0.79941527
O	-0.04471892	1.91425478	-0.25059554
O	-1.15737790	1.63296240	0.52915687
H	-1.82725261	1.39514710	-0.12287496
C	0.24478480	-1.08673704	0.63977977
H	0.20328381	-0.52696385	1.58621144
H	0.70952288	-2.05250394	0.89976375
C	1.05155875	-0.35287607	-0.39044464
H	0.47955343	0.86810472	-0.40083218
H	0.84992832	-0.67006275	-1.41459816
C	2.49402685	-0.10632143	-0.05287956
H	3.04867413	-1.05362515	-0.00802600
H	2.59275882	0.37865234	0.92275761
H	2.98025281	0.52496841	-0.79937853
H	-1.77765593	-1.95106719	0.95220976

Unscaled frequencies:

-2151.5	63.6	103.7	119.5	140.6	157.4	182.9	199.8
290.3	343.0	481.8	549.6	665.4	714.5	798.1	869.4
965.3	976.5	1058.1	1079.4	1125.0	1152.1	1172.7	1247.2
1296.1	1389.8	1400.5	1405.3	1422.9	1437.5	1464.1	1476.8
1479.0	1852.7	2940.9	2989.4	3013.7	3035.5	3090.1	3121.7
3136.5	3824.5						

Structure 7: zero-point-exclusive relative conformational energy = 0.80 kcal/mol

C	1.27530303	-1.19597292	0.24321779
O	2.19008627	-0.48810857	-0.08150645
O	0.05376061	1.64752426	0.70940484
O	0.47123191	1.77836541	-0.60661794
H	1.31899526	1.30815534	-0.61409278
C	-0.07049107	-1.19395687	-0.43323174
H	0.00338189	-0.64374559	-1.37624716
H	-0.35403481	-2.23369164	-0.65824026
C	-1.11750052	-0.56261093	0.45678022
H	-0.56521902	0.66005777	0.70994315
H	-1.18124255	-0.99032136	1.45952210
C	-2.42681861	-0.24847797	-0.20629362
H	-2.91117704	-1.16472702	-0.57096531
H	-2.26578738	0.40538780	-1.06958753
H	-3.11662924	0.24752649	0.47875985
H	1.38812564	-1.88477836	1.10782838

Unscaled frequencies:

-2247.7	53.6	81.6	135.1	158.2	186.6	199.0	229.8
340.9	376.8	522.7	545.3	601.4	797.1	848.8	916.4
963.6	1010.0	1058.5	1081.5	1127.5	1148.0	1160.3	1231.4
1272.4	1371.3	1400.5	1413.8	1446.3	1469.3	1474.4	1481.2
1488.0	1849.5	2944.0	3002.6	3011.9	3085.3	3096.2	3110.6
3138.5	3742.9						

Structure 9: zero-point-exclusive relative conformational energy = 1.42 kcal/mol

C	0.53371178	1.59310520	0.06662245
O	0.05030838	1.42462757	-1.01956310
O	-1.61715819	-1.17478803	-0.15358112
O	-2.16473533	0.04559675	0.21399346
H	-2.01519324	0.59009780	-0.56844904
C	0.84357104	0.50012298	1.05586309
H	1.82955610	0.72557670	1.49400154
H	0.12619374	0.63309113	1.87851446
C	0.80188804	-0.90658195	0.52340248
H	-0.48419022	-1.07905313	0.12066621
H	0.82956702	-1.65342573	1.31795084
C	1.66902046	-1.22977820	-0.66196806
H	2.72996864	-1.10539304	-0.40214855
H	1.45196056	-0.57304860	-1.50669443
H	1.53010557	-2.26426918	-0.98210214
H	0.76556511	2.62172568	0.41794747

Unscaled frequencies:

-2237.4	89.1	93.4	124.6	150.2	152.8	182.4	206.1
300.8	370.3	476.4	542.8	679.7	723.6	801.3	858.3
953.0	982.5	1054.3	1059.8	1105.2	1149.5	1164.8	1260.0
1346.1	1369.7	1396.4	1410.0	1424.4	1444.4	1463.3	1475.7
1487.2	1851.5	2938.1	2993.9	3010.3	3045.9	3104.6	3118.3
3149.5	3818.8						

Structure 11: zero-point-exclusive relative conformational energy = 1.85 kcal/mol

C	0.24010057	1.55149215	-0.17515245
O	-0.88558566	1.69521207	-0.57195474
O	-1.12092842	-1.40257437	-0.48753900
O	-2.02905325	-0.75030340	0.33268790
H	-2.03894623	0.14826125	-0.03192312
C	0.61289205	0.67456615	0.99505300

H	1.42670387	1.16413031	1.55057970
H	-0.25328155	0.58035103	1.65670312
C	1.06700992	-0.69611470	0.53508851
H	-0.09218003	-1.20638751	0.00725806
H	1.25183118	-1.38044277	1.36314614
C	2.06643367	-0.76152898	-0.58727584
H	2.99684274	-0.24212854	-0.31789701
H	1.68045275	-0.29129246	-1.49783195
H	2.32193763	-1.79453283	-0.82945249
H	1.07256110	2.07287946	-0.69241509

Unscaled frequencies:

-2299.4	53.7	114.4	137.8	147.0	189.3	204.6	251.0
292.7	425.0	511.0	570.0	624.4	755.2	846.3	901.0
973.8	988.0	1058.6	1073.6	1113.8	1145.0	1172.7	1250.9
1299.3	1355.0	1402.7	1420.8	1451.5	1468.8	1480.4	1485.5
1492.2	1848.0	2948.4	3007.4	3009.7	3082.6	3101.0	3126.1
3139.2	3736.9						

H. transition states leading to the formation of 4-oxo-1-butyl radical

Structure 1: zero-point-exclusive relative conformational energy = 0.0 kcal/mol

C	-0.313071	1.884364	0.032410
H	-1.097345	0.881635	0.541574
H	-0.061682	2.460224	0.923492
H	-1.026759	2.378075	-0.624356
C	0.827012	1.167542	-0.633432
H	0.451226	0.545233	-1.453379
H	1.494666	1.908159	-1.094014
C	1.623822	0.296129	0.338155
H	1.555084	0.668509	1.367848
H	2.697772	0.300403	0.103565
C	1.242015	-1.160244	0.351198
H	1.685839	-1.756650	1.175321
O	0.557439	-1.703556	-0.473977
O	-1.628038	-0.106828	0.803932
O	-2.017470	-0.606484	-0.429552
H	-1.272919	-1.177380	-0.673259

Unscaled frequencies:

-2334.8	35.1	82.9	102.5	170.5	186.7	236.9	287.0	
374.1	515.2	555.4	619.8	650.6	710.7	802.0	865.0	
963.4	971.8	1047.6	1060.7	1084.7	1136.0	1174.9	1252.5	
1254.7	1341.2	1389.9	1414.6	1434.2	1449.0	1456.2	1464.5	1488.1
1847.0	2955.9	3017.5	3029.8	3068.8	3078.6	3098.5	3194.5	3742.0

Structure 3: zero-point-exclusive relative conformational energy = 0.63 kcal/mol

C	0.614530	-1.623031	-0.456453
H	-0.563767	-1.240036	0.140048
H	0.393549	-1.362810	-1.492424
H	0.609327	-2.693825	-0.262720
C	1.698607	-0.827029	0.214038
H	1.637678	-0.951705	1.302628
H	2.681352	-1.223428	-0.075679
C	1.646267	0.663119	-0.145701
H	1.686767	0.810145	-1.228481
H	2.499884	1.179221	0.310192
C	0.392544	1.306159	0.379869
H	0.243637	1.245655	1.478377
O	-0.423844	1.855002	-0.314343
O	-1.469511	-0.771726	0.680806
O	-2.272573	-0.273717	-0.329918
H	-1.972691	0.645001	-0.414815

Unscaled frequencies:

-2379.7	41.5	97.0	156.1	166.5	205.7	217.8	296.2
397.4	508.4	514.6	574.9	588.2	783.1	798.9	907.3
954.1	959.2	1062.7	1077.4	1080.9	1153.0	1171.8	1232.0
1246.8	1336.1	1366.8	1416.7	1441.3	1450.7	1456.7	1464.0
1488.6	1838.3	2956.0	3016.3	3045.1	3056.3	3097.1	3115.0
3193.9	3727.3						

Structure 5: zero-point-exclusive relative conformational energy = 1.21 kcal/mol

C	-0.111676	-1.454577	-0.792133
H	0.945919	-1.126861	0.031715
H	0.102469	-2.475232	-1.100647
H	0.109228	-0.714003	-1.563047
C	-1.371923	-1.244630	0.001555
H	-2.240052	-1.267188	-0.675255
H	-1.518945	-2.064477	0.709603
C	-1.372323	0.081796	0.789343
H	-0.541432	0.095448	1.498510
H	-2.320641	0.185408	1.326315
C	-1.219620	1.235069	-0.156464
H	-2.117059	1.500332	-0.757023
O	-0.195092	1.843346	-0.325814
O	1.737245	-0.593248	0.677841
O	2.258457	0.380995	-0.159688
H	1.628887	1.111888	-0.062689

Unscaled frequencies:

-2391.3	91.4	98.0	133.8	154.6	188.8	218.6	265.0	
401.3	515.8	537.8	585.8	623.1	788.9	831.4	900.8	
962.8	976.9	1058.0	1067.2	1084.2	1143.8	1181.1	1223.1	
1263.3	1331.0	1360.6	1417.3	1454.3	1462.0	1466.2	1470.4	1495.8
1845.1	2936.0	2995.4	3060.8	3091.2	3098.3	3132.4	3194.7	3743.7

Structure 7: zero-point-exclusive relative conformational energy = 1.39 kcal/mol

C	-0.238773	1.407578	-0.805040
H	-1.319151	0.843523	-0.242573
H	-0.609466	2.373589	-1.143385
H	-0.077732	0.691655	-1.610652
C	0.833912	1.434129	0.250715
H	1.797556	1.615393	-0.246561
H	0.668434	2.266792	0.939550
C	0.927139	0.135520	1.048825
H	-0.007323	-0.072532	1.582163
H	1.706017	0.204624	1.820010
C	1.257249	-1.068798	0.209427
H	1.163999	-2.048529	0.724654
O	1.620293	-1.016144	-0.933834
O	-2.163688	0.159700	0.238906
O	-1.692670	-1.134016	0.037506
H	-2.110980	-1.401412	-0.787374

Unscaled frequencies:

-2122.5	66.4	109.7	136.2	165.0	168.8	225.2	247.3	371.4
421.6	563.0	596.6	671.7	718.0	811.1	864.9	950.5	965.1
1046.0	1056.0	1101.8	1132.1	1186.5	1232.7	1285.2	1357.3	1379.8
1412.7	1413.6	1438.8	1442.5	1447.4	1462.6	1853.2	2943.2	3016.1
3038.6	3088.4	3096.3	3104.5	3196.0	3848.1			

Structure 9: zero-point-exclusive relative conformational energy = 1.60 kcal/mol

C	-0.244055	1.415611	-0.045139
H	-1.260478	0.724743	-0.597547
H	-0.727492	2.332619	0.288387
H	0.415613	1.559284	-0.899988
C	0.268529	0.503384	1.032486
H	1.100466	1.004566	1.548686
H	-0.512296	0.329541	1.778950
C	0.752451	-0.835141	0.488625
H	-0.020600	-1.316029	-0.125282
H	0.962212	-1.545576	1.298962
C	2.008637	-0.732958	-0.332285
H	2.357793	-1.682931	-0.792703

O	2.630411	0.280542	-0.495766
O	-2.110636	-0.020197	-0.952264
O	-2.489617	-0.675706	0.215414
H	-3.269851	-0.188706	0.499354

Unscaled frequencies:

-2121.3	54.7	76.9	114.9	145.2	180.0	231.6	282.6	368.9
409.5	502.9	573.0	654.6	716.5	803.7	873.9	953.8	976.3
1047.7	1072.8	1106.2	1126.6	1165.7	1227.4	1283.5	1366.0	1379.8
1408.3	1412.9	1437.1	1439.6	1445.3	1456.5	1854.8	2932.4	3011.9
3037.9	3076.1	3087.6	3105.3	3195.4	3843.9			

Structure 11: zero-point-exclusive relative conformational energy = 1.93 kcal/mol

C	-0.995918	1.615960	-0.090791
H	-1.837032	0.598537	0.200289
H	-1.016078	2.174450	0.845973
H	-1.505565	2.126742	-0.906250
C	0.295051	0.933310	-0.427792
H	0.167465	0.274441	-1.293144
H	1.041424	1.678931	-0.739123
C	0.845808	0.125258	0.737401
H	0.139163	-0.658594	1.041146
H	0.990631	0.750677	1.629705
C	2.160402	-0.532885	0.426845
H	2.589901	-1.157115	1.240699
O	2.740547	-0.417025	-0.616566
O	-2.430837	-0.397604	0.418329
O	-1.812853	-1.343439	-0.391976
H	-2.376820	-1.373389	-1.171569

Unscaled frequencies:

-2164.5	39.7	77.4	110.1	158.2	189.6	198.6	251.0	348.1
404.0	500.9	567.6	658.9	704.1	805.8	869.4	961.7	968.6
1051.1	1082.6	1113.0	1147.7	1165.2	1220.6	1291.0	1321.5	1399.2
1406.7	1410.4	1440.8	1443.7	1453.7	1457.6	1858.0	2930.3	3012.1
3027.8	3067.7	3082.2	3095.3	3186.1	3843.1			

M08-HX/maug-cc-pVTZ optimized Cartesian coordinates (in Å) of the structure of hydroperoxyl radical and hydrogen peroxide.

A. Hydroperoxyl radical

O	0.054779000	0.706842000	0.000000000
O	0.054779000	-0.598359000	0.000000000
H	-0.876470000	-0.867868000	0.000000000

B. Hydrogen peroxide.

O	0.00000000	0.71145346	-0.05703296
O	0.00000000	-0.71145346	-0.05703296
H	-0.79006051	-0.90326379	0.45626364
H	0.79006051	0.90326379	0.45626364

Validation of density functionals

We optimized the geometries of all structures of butanal, butanoyl radical, 1-oxo-2-butyl radical, 4-oxo-2-butyl radical, the transition states, the hydroperoxyl radical, and hydrogen peroxide with the M06-2X, M08-SO, and M08-HX density functionals using three basis sets, viz. MG3S (which is the same as 6-311+G(2df,2p) for H, C and O), ma-TZVP, and maug-cc-pVTZ. The reason we chose these density functionals is because of their good performance for reactive barrier heights.

Coupled cluster (CCSD(T)-F12a) single-point calculations were then performed on the M08-HX/MG3S optimized geometries using the jun-cc-pVDZ and jun-cc-pVTZ one-electron basis sets plus explicitly correlated quasi-double excitations treated by the F12a approximation. Note that because the explicitly correlated excitations are included, the jun-cc-pVTZ results are essentially at the complete basis set limit, and hence CCSD(T)-F12a/jun-cc-pVTZ will also be called CCSD(T)/CBS. We also tested the jun-jun dual-level method for the coupled cluster calculations.

The geometry optimizations were performed using the *Gaussian 09* program with the *MN-GFM* module, and the coupled cluster calculations were done with *Molpro*.

Table S1 lists the zero-point-exclusive forward barrier height ($V_f^\ddagger$), reverse barrier height ($V_r^\ddagger$), and energy of reaction (ΔU) for the three abstraction channels. The structures of reactant, product, and saddle points used are those listed in Table S5 and Table S6 respectively. In particular, butanal is structure 6; butanoyl radical is structure 6; 1-oxo-2-butyl radical is structure 1; 4-oxo-2-butyl radical is 1; TS of R1 is structure 27; TS of R2 is structure 1; and TS of R3 is structure 3. Errors calculated in this table are defined as differences from the CCSD(T)/CBS benchmark. Mean unsigned errors (MUEs) for each abstraction site are averages over the forward and reverse barrier heights and the energy of reaction. Average MUEs are then averaged over the three sites. The table shows that for the H atom abstraction from the carbonyl-C of butanal, the MUE is smallest (0.96 kcal/mol) for M08-HX/maug-cc-pVTZ. For the abstraction of H atom from α-C of butanal, we found that M08-SO/maug-cc-pVTZ method gives the smallest MUE (0.18 kcal/mol). For the β-H abstraction, the MUE is lowest for M08-HX/MG3S (0.22 kcal/mol). Since we found a different method to have the lowest MUE value for each site of H atom abstraction, we take an average of the MUEs, and we find that M08-HX/maug-cc-pVTZ method, with an average MUE of 0.58 kcal/mol, performs the best. Hence, we chose the M08-HX/maug-cc-pVTZ method for further calculations.

Structure search. After the validations of the density functional results, we performed structure searches. We generated initial guesses for all the structures of butanal, butanoyl radical, 1-oxo-2-butyl radical, 4-oxo-2-butyl radical, and the transition states. The geometry optimizations were performed with the M08-HX/maug-cc-pVTZ method using the ultrafine density functional integration grid in the *Gaussian 09* program with *MN-GFM*. Then the distinct optimized geometries were further optimized, and vibrational frequency calculations were carried out with a density functional integration grid of 99 radial shells and 974 angular points per shell.

Table S1. Forward and reverse classicala barrier heights and classical energies of reaction (in kcal/mol) for the H-abstraction from different carbons of butanal[b]

Electronic model chemistry	$V^{\ddagger}$	$V^{\ddagger}_{\mathrm{r}}$	ΔU	MUE[c]
Abstraction of H atom from carbonyl-C to yield butanoyl radical				
M06-2X/MG3S	10.59	8.20	2.39	1.80
M08-HX/MG3S	11.60	8.88	2.72	1.35
M08-SO/MG3S	12.30	9.04	3.26	1.25
M06-2X/ma-TZVP	11.29	8.35	2.94	1.70
M08-HX/ma-TZVP	12.81	9.35	3.46	1.39
M08-SO/ma-TZVP	13.51	9.10	4.41	2.02
M06-2X/maug-cc-pVTZ	10.58	8.42	2.16	1.65
M08-HX/maug-cc-pVTZ	12.05	9.46	2.59	0.96
M08-SO/maug-cc-pVTZ	12.96	9.41	3.55	1.45
CCSD(T)-F12a/jun-cc-pVDZ[b]	12.11	10.39	1.72	0.34
jun-jun[b]	12.53	11.60	0.93	0.47
CCSD(T)/CBS[b]	12.28	10.90	1.38	0.00
Abstraction of H atom from α-C to yield 1-oxo-2-butyl radical				
M06-2X/MG3S	13.91	11.34	2.57	1.74
M08-HX/MG3S	15.28	12.16	3.12	0.92
M08-SO/MG3S	15.41	12.97	2.44	0.74
M06-2X/ma-TZVP	14.88	11.61	3.27	1.29
M08-HX/ma-TZVP	17.10	12.93	4.17	0.79
M08-SO/ma-TZVP	17.22	13.24	3.98	0.67
M06-2X/maug-cc-pVTZ	14.17	12.01	2.16	1.57
M08-HX/maug-cc-pVTZ	16.01	13.17	2.84	0.34
M08-SO/maug-cc-pVTZ	16.74	13.81	2.93	0.18
CCSD(T)-F12a/jun-cc-pVDZ[b]	16.57	12.88	3.69	0.47
jun-jun[b]	16.86	13.41	2.45	0.33
CCSD(T)/ CBS[b]	16.52	13.54	2.98	0.00
Abstraction of H atom from β-C to yield 4-oxo-2-butyl radical				
M06-2X/MG3S	15.01	2.78	12.23	1.23
M08-HX/MG3S	16.51	4.47	12.04	0.22
M08-SO/MG3S	16.86	5.28	11.58	0.43
M06-2X/ma-TZVP	15.91	3.06	12.85	1.05
M08-HX/ma-TZVP	18.20	5.16	13.04	0.91

M08-SO/ma-TZVP	18.62	5.65	12.97	1.19
M06-2X/maug-cc-pVTZ	15.11	3.34	11.77	1.15
M08-HX/maug-cc-pVTZ	17.06	5.28	11.78	0.43
M08-SO/maug-cc-pVTZ	18.07	6.00	12.07	0.91
CCSD(T)-F12a/jun-cc-pVDZ[b]	16.90	4.02	12.88	0.45
jun-jun[b]	16.23	4.58	11.65	0.41
CCSD(T) / CBS[b]	16.84	4.63	12.21	0.00

$$\text{Average MUE} = \frac{1}{3}\left(\text{MUE}_{>\text{C=O}} + \text{MUE}_{\alpha} + \text{MUE}_{\beta}\right)^{c}$$

M06-2X/MG3S	1.59
M08-HX/MG3S	0.83
M08-SO/MG3S	0.81
M06-2X/ma-TZVP	1.34
M08-HX/ ma-TZVP	1.03
M08-SO/ ma-TZVP	1.29
M06-2X/ maug-cc-pVTZ	1.46
M08-HX/ maug-cc-pVTZ	0.58
M08-SO/ maug-cc-pVTZ	0.85
CCSD(T)-F12a/jun-cc-pVDZ[b]	0.42
jun-jun[b]	0.40
CCSD(T)/CBS[b]	0.00

[a] In the context of the present table, "classical" means zero-point-exclusive.

[b] In order to perform a consistent comparison, the coupled cluster results in this table are all calculated at geometries obtained by the M08-HX/maug-cc-pVTZ method.

[c] The mean unsigned errors are calculated with respect to CCSD(T)-F12a/jun-cc-pVTZ method, which is labeled as CCSD(T)/CBS.

Table S2. Multi-structural torsional anharmonicity factors for the H-atom abstraction from different carbons of butanal by •O2H[a,b]

T (K)	Multi-structural anharmonicity factors														
	$F_{\text{MS-T}}^{\text{R}}$	$F_{\text{MS-T}}^{\text{P1}}$	$F_{\text{MS-T}}^{\text{P2}}$	$F_{\text{MS-T}}^{\text{P3}}$	$F_{\text{MS-T}}^{\text{H}_2\text{O}_2}$	$F_{\text{MS-T}}^{\ddagger,1}$	$F_{\text{MS-T}}^{\ddagger,2}$	$F_{\text{MS-T}}^{\ddagger,3}$	$F_{\text{f, R1}}^{\text{MS-T}}$	$F_{\text{r, R1}}^{\text{MS-T}}$	$F_{\text{f, R2}}^{\text{MS-T}}$	$F_{\text{r, R2}}^{\text{MS-T}}$	$F_{\text{f, R3}}^{\text{MS-T}}$	$F_{\text{r, R3}}^{\text{MS-T}}$	$F_{\text{f, R4}}^{\text{MS-T}}$
200	4.76	10.02	2.78	1.92	2.08	28.97	4.08	6.93	6.09	1.39	0.86	0.70	1.46	1.73	0.53
250	5.64	11.14	3.03	2.26	2.11	40.84	6.63	9.48	7.24	1.74	1.18	1.04	1.68	1.99	0.54
298.15	6.58	12.04	3.25	2.56	2.14	53.15	10.48	13.29	8.07	2.06	1.59	1.51	2.02	2.43	0.62
300	6.62	12.07	3.26	2.57	2.14	53.63	10.65	13.47	8.10	2.08	1.61	1.53	2.03	2.45	0.62
400	8.64	13.47	3.65	3.03	2.20	79.81	23.58	29.18	9.24	2.69	2.73	2.93	3.38	4.37	1.01
500	10.48	14.40	3.95	3.31	2.26	104.19	42.50	59.19	9.94	3.21	4.05	4.76	5.65	7.92	1.75
600	12.02	14.96	4.18	3.44	2.30	125.07	65.89	104.15	10.41	3.64	5.48	6.86	8.67	13.17	2.77
800	14.14	15.30	4.46	3.44	2.34	154.70	119.42	224.50	10.94	4.32	8.44	11.43	15.87	27.85	5.28
1000	15.22	15.01	4.59	3.27	2.35	169.82	173.22	353.45	11.16	4.82	11.38	16.11	23.22	46.02	7.94
1300	15.59	14.04	4.58	2.92	2.32	173.59	241.23	507.51	11.14	5.34	15.47	22.75	32.55	75.01	11.44
1500	15.35	13.27	4.50	2.68	2.28	168.51	274.84	572.43	10.98	5.57	17.90	26.77	37.28	93.53	13.30
1800	14.65	12.10	4.32	2.36	2.22	155.37	307.85	619.29	10.61	5.79	21.02	32.08	42.28	118.32	15.38
2000	14.06	11.35	4.18	2.17	2.18	145.01	319.94	625.17	10.31	5.87	22.75	35.16	44.46	132.60	16.35
2400	12.82	10.00	3.88	1.84	2.09	123.97	326.38	599.79	9.67	5.93	25.46	40.28	46.79	155.81	17.57

[a] P1: butanoyl radical, P2: 1-oxo-2-butyl radical, P3: 4-oxo-2-butyl radical. [b] $F_{\text{reverse, R1}}^{\text{MS-T}} = \dfrac{F_{\text{MS-T}}^{\ddagger,1}}{F_{\text{MS-T}}^{\text{P1}} F_{\text{MS-T}}^{\text{H}_2\text{O}_2}}$, $F_{\text{reverse, R2}}^{\text{MS-T}} = \dfrac{F_{\text{MS-T}}^{\ddagger,2}}{F_{\text{MS-T}}^{\text{P2}} F_{\text{MS-T}}^{\text{H}_2\text{O}_2}}$, $F_{\text{reverse, R3}}^{\text{MS-T}} = \dfrac{F_{\text{MS-T}}^{\ddagger,3}}{F_{\text{MS-T}}^{\text{P3}} F_{\text{MS-T}}^{\text{H}_2\text{O}_2}}$

Table S3. Forward and reverse SS-VTST and MS-VTST thermal rate constants (in cm^3 molecule^{-1} s^{-1}) for the H-abstraction from the carbonyl carbon and from the α-C and β-C of butanal by •O2H, the activation energies, E_a (in kcal/mol) of the forward and reverse reactions, and SCT representative tunneling energy (in kcal/mol)[a]

T (K)	Forward rate coefficients		E_a for the forward reaction	Reverse rate coefficients		E_a for the reverse reaction	SCT representative tunneling energy
	$k^{\text{SS-CVT/SCT}}$	$k^{\text{MS-CVT/SCT}}$		$k^{\text{SS-CVT/SCT}}$	$k^{\text{MS-CVT/SCT}}$		
Reaction R1: $CH_3CH_2CH_2CH{=}O + {\bullet}O_2H \rightarrow CH_3CH_2CH_2{\bullet}C{=}O + H_2O_2$							
200	4.69E-22	2.86E-21	4.12	9.85E-19	1.37E-18	1.33	78.63
250	5.44E-21	3.94E-20	5.60	1.99E-18	3.45E-18	2.27	80.25
298.15	3.52E-20	2.84E-19	6.78	4.07E-18	8.40E-18	3.22	80.32
300	3.75E-20	3.04E-19	6.82	4.19E-18	8.69E-18	3.26	80.33
400	7.36E-19	6.80E-18	8.64	1.78E-17	4.79E-17	5.08	82.69
500	6.75E-18	6.71E-17	9.93	6.32E-17	2.02E-16	6.57	84.02
600	3.75E-17	3.90E-16	10.97	1.83E-16	6.65E-16	7.79	84.9
800	4.53E-16	4.96E-15	12.76	9.53E-16	4.12E-15	9.74	85.08
1000	2.60E-15	2.90E-14	14.42	3.26E-15	1.57E-14	11.40	85.46
1300	1.65E-14	1.84E-13	16.89	1.29E-14	6.87E-14	13.74	85.63
1500	4.22E-14	4.63E-13	18.54	2.67E-14	1.49E-13	15.27	85.69
1800	1.25E-13	1.33E-12	21.04	6.34E-14	3.67E-13	17.57	85.69
2000	2.25E-13	2.32E-12	22.73	1.02E-13	5.99E-13	19.11	85.69
2400	5.86E-13	5.67E-12	26.11	2.25E-13	1.34E-12	22.23	85.69
Reaction R2: $CH_3CH_2CH_2CH{=}O + {\bullet}O_2H \rightarrow CH_3CH_2{\bullet}CHCH{=}O + H_2O_2$							
200	1.15E-25	9.85E-26	5.54	4.03E-22	2.84E-22	2.33	78.83
250	2.63E-24	3.09E-24	7.64	1.25E-21	1.30E-21	3.86	81.24
298.15	3.04E-23	4.84E-23	9.35	3.92E-21	5.90E-21	5.32	82.17
300	3.31E-23	5.33E-23	9.41	4.09E-21	6.25E-21	5.37	82.17
400	1.57E-21	4.28E-21	12.05	3.43E-20	1.00E-19	7.97	83.56
500	2.58E-20	1.05E-19	13.91	1.93E-19	9.18E-19	9.97	84.86
600	2.20E-19	1.21E-18	15.39	7.85E-19	5.38E-18	11.52	85.63
800	4.86E-18	4.10E-17	17.86	6.69E-18	7.65E-17	13.97	87.46
1000	4.19E-17	4.77E-16	20.12	3.20E-17	5.16E-16	16.04	89.23
1300	4.06E-16	6.28E-15	23.46	1.79E-16	4.07E-15	18.98	89.59
1500	1.25E-15	2.23E-14	25.69	4.29E-16	1.15E-14	20.92	89.59
1800	4.66E-15	9.79E-14	29.07	1.23E-15	3.95E-14	23.85	89.59
2000	9.48E-15	2.16E-13	31.33	2.20E-15	7.74E-14	25.81	89.59
2400	2.99E-14	7.62E-13	35.91	5.72E-15	2.30E-13	29.79	89.59
Reaction R3: $CH_3CH_2CH_2CH{=}O + {\bullet}O_2H \rightarrow CH_3{\bullet}CHCH_2CH{=}O + H_2O_2$							

200	7.91E-30	1.15E-29	10.72	1.61E-18	2.79E-18	0.65	76.58
250	3.74E-27	6.30E-27	13.01	2.12E-18	4.21E-18	1.32	76.58
298.15	2.43E-25	4.91E-25	14.50	2.94E-18	7.14E-18	2.12	78.41
300	2.79E-25	5.68E-25	14.55	2.98E-18	7.30E-18	2.15	78.43
400	8.79E-23	2.97E-22	16.45	6.01E-18	2.63E-17	3.99	79.05
500	3.70E-21	2.09E-20	17.67	1.15E-17	9.09E-17	5.72	79.12
600	5.39E-20	4.67E-19	18.65	2.05E-17	2.70E-16	7.19	79.55
800	2.02E-18	3.20E-17	20.44	5.30E-17	1.48E-15	5.47	80.5
1000	2.21E-17	5.14E-16	22.22	1.14E-16	5.23E-15	6.89	80.91
1300	2.52E-16	8.21E-15	24.99	2.82E-16	2.12E-14	8.90	80.96
1500	8.19E-16	3.05E-14	26.88	4.63E-16	4.33E-14	10.21	80.96
1800	3.22E-15	1.36E-13	29.79	8.69E-16	1.03E-13	12.18	80.96
2000	6.69E-15	2.97E-13	31.75	1.25E-15	1.65E-13	13.49	80.96
2400	2.16E-14	1.01E-12	35.73	2.31E-15	3.60E-13	16.13	80.96

[a] Includes variational effects, multi-structural torsional anharmonicity, and tunneling

Table S4. Sequence number, structures, relative conformational energies (in kcal/mol), and $M_{j,\tau}$ obtained with M08-HX/MG3S electronic model chemistry of butanal, butanoyl radical, 1-oxo-2-butyl radical, and 4-oxo-2-butyl radical.

Number j	Structures	Relative conformational energy		$M_{j,\tau}$
		zero-point-exclusive	zero-point-inclusive	
		butanal		
1, 2	$\mathbf{C^{-}G^{-}, C^{+}G^{+}}$	0.00	0.04	2.57
3	**CT**	0.09	0.00	3.08
4, 5	$\mathbf{A^{+}G^{-}, A^{-}G^{+}}$	1.04	0.95	2.44
6, 7	$\mathbf{A^{-}T^{-}, A^{+}T^{+}}$	1.20	1.10	2.79
		butanoyl radical		
1, 2	$\mathbf{C^{+}G^{+}, C^{-}G^{-}}$	0.00	0.01	2.46
3	**CT**	0.11	0.00	2.81
4, 5	$\mathbf{T^{-}G^{+}, T^{+}G^{-}}$	0.28	0.06	2.48
6, 7	$\mathbf{A^{-}T^{-}, A^{+}T^{+}}$	0.71	0.43	3.02
		1-oxo-2-butyl radical		
1, 2	$\mathbf{C^{-}A^{+}, C^{+}A^{-}}$	0.00	0.00	2.50
3, 4	$\mathbf{T^{+}A^{+}, T^{-}A^{-}}$	0.76	0.62	2.47
5	**TC**	1.32	1.33	2.39
6	**CC**	1.92	1.91	2.34
		4-oxo-2-butyl radical		
1	**CT**	0.00	0.00	2.89
2, 3	$\mathbf{C^{-}G^{+}, C^{+}G^{-}}$	0.32	0.75	2.64
4, 5	$\mathbf{a^{-}g^{+}, a^{+}g^{-}}$	0.37	0.86	2.45
6, 7	$\mathbf{A^{-}T^{+}, A^{+}T^{-}}$	1.13	1.21	2.77

Table S5. Sequence number, strongly coupled dihedrals, the relative conformational energies (in kcal/mol), and $M_{j,\tau}$ obtained with M08-HX/MG3S electronic model chemistry of the transition states. The numbering of the dihedrals are in Figures 1(b), 1(d), 1(f), and 1(h).[a]

Number j	D_1	D_2	D_3	D_4	D_5	Relative conformational energy		$M_{j,\tau}$
						Zero-point-exclusive	Zero-point-inclusive	
				transition states leading to the formation of butanoyl radical (R1)				
	(5-1-2-3)	(1-2-3-4)	(5-1-8-6)	(1-8-6-7)	(8-6-7-9)			
1, 2	-141.5	59.2	58.8	-9.6	-89.9	0.00	0.00	2.26
3, 4	-127.2	62.6	119.8	-33.6	-94.8	0.32	0.34	2.34
5, 6	6.4	69.9	7.0	21.2	-89.9	0.33	0.17	2.06
7, 8	-6.4	-69.9	7.6	20.5	-90.0	0.34	0.21	2.05
9, 10	132.2	-59.0	156.6	-22.4	-97.8	0.42	0.43	2.20
11, 12	0.2	-179.8	7.1	21.3	-89.7	0.43	0.15	2.07
13, 14	-9.1	-69.5	150.4	-29.5	-97.1	0.47	0.43	2.19
15, 16	2.9	70.4	149.9	-31.3	-97.3	0.56	0.53	2.21
17, 18	-3.8	179.3	150.7	-30.8	-97.2	0.62	0.46	2.14
19, 20	155.6	-62.6	-7.5	34.8	-91.4	0.66	0.34	2.03
21, 22	123.6	176.5	166.8	-24.0	-98.5	0.69	0.71	2.27
23, 24	-128.3	-175.3	20.4	10.2	-90.4	1.11	0.86	2.20
25, 26	-89.7	-56.8	41.6	6.8	-89.9	1.11	1.24	2.21
27, 28	-121.9	-176.1	120.6	-36.9	-93.9	1.12	1.02	2.23
29, 30	136.5	175.4	8.9	20.0	-90.7	1.18	0.89	2.18
31, 32	123.0	64.8	2.3	24.3	-89.7	1.30	1.22	2.14
33, 34	-95.1	-60.7	-173.1	20.4	99.8	1.34	1.47	2.33
35, 36	-84.7	-66.7	-175.1	-4.6	-99.4	1.63	1.77	2.27

37, 38	137.8	-61.8	-145.2	58.1	-100.4	1.73	1.66	2.08
39, 40	-122.3	-173.5	-154.9	-5.2	-104.1	1.75	1.66	2.29
41, 42	-89.3	-54.3	168.1	-110.7	99.0	2.55	2.76	1.78
43, 44	-115.5	66.4	-156.2	5.1	-104.2	2.56	1.51	2.17
45, 46	148.4	179.6	-128.3	32.6	-100.3	2.58	2.39	2.29

transition states leading to the formation of 1-oxo-2-butyl radical (R2)

	(5-1-2-3)	(1-2-3-4)	(1-2-9-6)	(2-9-6-7)	(9-6-7-8)			
1, 2	-25.5	158.1	-52.0	-28.4	81.4	0.00	0.00	1.98
3, 4	-22.7	-69.5	-42.9	-33.9	83.8	0.77	0.81	1.82
5, 6	-24.4	162.6	-65.0	74.2	-87.1	1.15	1.01	1.87
7, 8	-21.3	-73.6	-58.5	65.5	-88.8	1.39	1.26	1.79
9, 10	170.9	160.6	29.0	-42.2	86.5	1.69	1.31	1.95
11, 12	172.9	160.9	50.8	30.8	-77.9	1.85	1.56	1.98
13, 14	-4.1	68.7	-46.6	22.3	-90.3	1.85	1.73	2.03
15, 16	170.0	-77.7	38.5	-52.0	86.8	1.96	1.62	1.79
17, 18	171.8	-78.2	50.5	31.0	-78.2	2.02	1.82	1.86
19, 20	-7.8	175.2	-122.2	42.4	-96.6	2.19	1.79	2.20
21, 22	179.3	64.5	5.5	-27.8	86.3	2.20	1.87	1.97
23, 24	178.3	65.4	47.5	33.8	-76.9	2.57	2.35	1.93
25, 26	-10.1	163.1	159.2	-21.4	94.4	2.59	2.34	1.91
27, 28	-9.4	-77.0	-168.2	-5.6	-98.5	2.86	2.53	2.23
29, 30	154.8	171.4	-116.3	30.6	98.0	2.89	2.42	1.98
31, 32	-7.2	70.7	-17.2	-28.4	97.2	2.91	2.65	1.95
33, 34	-9.8	171.5	171.5	-31.0	-98.7	2.92	2.41	2.10
35, 36	-3.2	60.2	-165.7	-6.2	95.4	2.96	2.69	2.09
37, 38	152.1	173.9	-113.0	29.7	-99.1	3.21	2.73	2.09
39, 40	-10.0	-74.7	159.1	-35.9	-99.3	3.25	2.77	1.94
41, 42	-2.4	64.0	-176.0	9.1	-98.6	3.28	2.95	2.17
43, 44	155.8	169.0	163.5	-28.1	-94.8	3.34	2.73	2.07
45, 46	153.9	-80.6	-159.1	-16.0	-96.5	3.59	3.06	2.01
47, 48	-2.9	68.6	146.4	-19.9	98.6	3.67	3.23	2.02
49, 50	-3.5	69.3	147.4	-35.4	-99.2	3.72	3.28	1.99

51, 52	154.2	-77.1	-143.8	39.5	98.2	3.74	3.15	1.81
53, 54	152.0	46.8	-140.4	-14.9	-97.2	3.76	3.43	2.05
55, 56	152.0	161.9	166.8	-29.7	96.1	4.17	3.78	2.03
57, 58	151.9	42.9	-134.9	-21.0	99.2	4.18	3.85	2.00
59, 60	158.2	67.9	-57.3	29.8	-97.4	4.78	4.53	2.06

transition states leading to the formation of 4-oxo-2-butyl radical (R3)

	(5-1-2-3)	(1-2-3-4)	(2-3-11-6)	(3-11-6-7)	(11-6-7-8)			
1, 2	5.1	62.2	79.4	26.5	-77.9	0.00	0.00	2.07
3, 4	-1.1	177.4	-61.3	-51.0	78.0	0.33	0.22	1.92
5, 6	-3.4	-177.5	34.4	-45.4	-86.8	0.70	0.38	2.02
7, 8	-108.2	168.0	18.8	23.3	-89.9	0.80	0.97	2.02
9, 10	13.0	55.8	-35.7	33.9	86.3	1.42	1.24	1.98
11, 12	96.3	47.3	29.7	-62.8	87.4	1.85	2.13	1.88
13, 14	-1.7	-69.7	50.0	12.8	97.9	2.14	1.91	2.23
15, 16	-64.7	78.0	41.7	66.5	-88.4	2.25	2.44	1.93
17, 18	7.1	-175.8	47.3	19.3	98.3	2.53	2.25	2.21
19, 20	-1.0	-75.7	-22.4	-29.0	-97.6	2.53	2.18	2.04
21, 22	-2.2	-72.5	60.4	-4.4	-102.0	2.91	2.63	2.50
23, 24	-115.9	176.2	-26.6	-49.4	96.1	3.06	2.73	1.95
25, 26	-0.8	-71.6	104.9	50.9	-98.4	3.22	2.68	1.98
27, 28	130.8	175.9	44.8	17.7	98.7	3.28	2.97	2.14
29, 30	16.1	177.6	22.9	-8.6	101.6	3.44	3.01	2.57
31, 32	-129.9	53.6	68.5	27.1	97.9	3.47	3.09	2.10
33, 34	-131.2	53.2	15.2	-44.8	-99.1	3.48	3.20	1.94
35, 36	93.0	-71.1	53.1	6.9	98.9	3.55	3.35	2.11
37, 38	134.3	168.9	57.5	-10.0	-103.8	3.86	3.43	1.98
39, 40	99.8	-72.7	59.4	1.5	-100.0	3.88	3.66	2.39
41, 42	97.9	-77.0	-28.0	-24.2	-98.9	3.95	3.64	1.89
43, 44	-117.2	-63.2	59.2	4.5	99.7	4.14	3.96	2.22
45, 46	-141.9	53.9	-8.0	-21.7	105.3	4.21	3.83	2.38
47, 48	-120.5	-69.7	68.0	-14.1	-100.7	4.24	4.04	2.15
49, 50	98.0	-72.1	113.0	38.0	-98.4	4.28	3.84	1.92

51, 52	-0.1	59.4	-51.5	-19.3	-98.2	4.31	4.00	2.76
53, 54	-10.8	62.8	-31.4	8.4	-100.8	4.38	4.03	2.24
55, 56	0.5	64.2	-67.9	-43.2	-98.1	4.55	4.08	1.90
57, 58	-116.2	-66.1	128.7	38.8	98.3	4.68	4.30	1.93
59, 60	120.6	169.2	-90.1	-18.4	100.1	4.99	4.44	1.88
61, 62	-117.9	-67.4	109.5	39.6	-100.0	4.99	4.54	1.98
63, 64	-132.7	58.3	-63.0	-50.9	100.9	5.03	4.39	1.88
65, 66	4.0	64.9	-167.4	3.0	99.6	5.04	4.58	2.11
67, 68	2.9	65.5	-116.1	-6.9	101.2	5.05	4.48	2.32
69, 70	-145.3	179.5	143.0	31.2	99.3	5.06	4.38	1.87
71, 72	-1.9	58.6	134.1	-22.4	98.4	5.13	4.61	2.03

transition states leading to the formation of 4-oxo-1-butyl radical (R4)

	(13-11-8-5)	(11-8-5-1)	(8-5-1-2)	(5-1-2-14)	(1-2-14-15)	(2-14-15-16)	V	$V+ZPE$	$M_{j,\tau}$
1, 2	13.5	97.0	-59.7	-18.2	-50.4	92.6	0.00	0.00	2.31
3, 4	-121.1	65.4	-69.9	23.8	99.7	-92.6	0.63	0.69	2.06
5, 6	-102.7	59.2	44.9	-72.1	-52.0	84.2	1.21	1.54	2.22
7, 8	11.1	61.0	43.3	-73.3	-8.5	-94.0	1.39	1.42	2.35
9, 10	4.0	69.0	59.8	0.3	32.5	97.3	1.60	1.36	2.83
11, 12	1.6	-178.3	-61.2	-0.3	-28.6	-97.0	1.93	1.53	3.07
13, 14	1.3	-174.5	-55.1	59.1	33.3	98.2	2.71	2.27	2.49
15, 16	-3.9	-71.4	-63.9	-6.9	-33.8	102.8	2.94	2.58	2.65
17, 18	-105.7	50.8	44.1	-143.4	125.7	-79.7	3.09	3.25	1.78
19, 20	-97.9	69.1	-87.4	-78.9	96.3	90.5	3.29	3.20	1.97
21, 22	-1.4	178.1	-64.5	-10.9	-38.3	101.4	3.33	2.80	2.69
23, 24	-3.0	-69.8	174.6	-21.7	-15.7	-95.2	3.55	3.17	2.56
25, 26	124.7	173.4	-63.1	-0.4	-30.6	-98.5	3.58	3.15	2.75
27, 28	15.4	80.6	-29.8	80.6	22.0	98.1	3.62	3.49	2.55
29, 30	-1.8	-67.9	-167.6	36.8	18.8	98.1	3.79	3.38	2.53
31, 32	-0.9	179.1	176.6	-7.5	-30.8	97.9	3.99	3.47	2.67
33, 34	-133.7	65.2	-76.9	-29.5	-14.4	-98.6	4.05	3.70	2.83
35, 36	-114.1	69.0	65.1	4.3	26.1	98.9	4.19	3.80	2.70
37, 38	133.4	170.9	61.1	5.7	26.3	99.1	4.41	3.89	2.47

39, 40	124.3	174.9	-62.7	37.7	56.3	97.7	4.52	3.96	2.29
41, 42	0.1	-179.9	174.2	-29.4	-16.9	-98.9	4.52	3.91	3.76
43, 44	-121.2	69.1	69.8	16.6	9.3	-103.0	4.68	4.17	2.66
45, 46	127.8	172.8	-67.2	-14.6	-18.5	105.8	4.83	4.31	3.04
47, 48	0.7	-179.2	-176.2	97.8	25.3	99.1	4.97	4.30	2.07
49, 50	131.5	65.8	-80.3	-26.4	12.1	-100.5	4.99	4.73	2.73
51, 52	128.1	168.6	54.5	-62.4	-28.3	-99.2	5.08	4.54	2.78
53, 54	-12.8	-79.2	35.8	-98.1	-48.6	101.8	5.20	4.82	2.19
55, 56	-132.1	64.4	-78.8	-48.7	-0.4	105.9	5.21	4.65	2.77
57, 58	-116.9	67.7	-168.2	33.4	21.5	97.7	5.22	4.74	2.42
59, 60	-125.2	64.5	172.4	-28.0	-24.0	-98.2	5.29	4.74	2.48
61, 62	-123.4	-176.4	174.2	-10.2	26.4	99.6	5.38	4.82	2.49
63, 64	-126.6	-175.8	171.4	-31.3	-21.5	-98.8	5.39	4.87	2.51
65, 66	-150.6	-90.3	57.1	-82.5	6.1	-100.0	5.40	4.96	2.20
67, 68	131.4	168.4	51.5	-75.1	-21.9	100.9	5.44	4.94	2.34
69, 70	127.9	63.5	162.0	-30.4	-19.1	-98.6	6.02	5.55	2.49
71, 72	121.7	62.9	164.8	-11.1	20.9	99.0	6.10	5.57	2.46
73,74	123.9	68.0	-71.2	-102.6	-32.7	100.3	6.15	5.59	2.11
75,76	1.3	64.5	-109.4	-62.2	45.9	-100.9	6.31	5.85	2.18

[a] In each case there are two mirror image structures that have identical dihedral angles with different sign and the same energies.

Further details of anharmonicity factors

The anharmonicity factors $F^{\chi}_{\text{MS-T}}$ of eq 12 can be factored as

$$F^{\chi}_{\text{MS-T}} = F^{\chi}_{\text{MS-LH}}(T) F^{\chi}_{\text{T}}(T) \tag{S1}$$

where χ is R or ‡, MS-LH denotes the multiple-structure local harmonic approximation, and F^{χ}_{T} accounts for torsional (T) anharmonicity. We calculate the MS-LH and T factors in terms of partition functions, Q, as follows:

$$F^{\chi}_{\text{MS-LH}} = \frac{Q^{\text{MS-LH}}_{\chi,\,\text{con-rovib}}(T)}{Q^{\text{SS-HO}}_{\chi,\,\text{rovib, GM}}(T)} \tag{S2}$$

$$F^{\chi}_{\text{T}} = \frac{Q^{\text{MS-T}}_{\chi,\,\text{con-rovib}}(T)}{Q^{\text{MS-LH}}_{\chi,\,\text{con-rovib}}(T)} \tag{S3}$$

where the term “con” and “rovib” denote conformational and rotational-vibrational respectively, GM denotes the global minimum geometry of reacting species or the transition state (‡), and SS-HO denotes the single-structure harmonic oscillator approximation. Since $k^{\text{SS-CVT/SCT}}$, $Q^{\text{SS-HO}}_{\chi,\,\text{rovib, GM}}$, and $Q^{\text{MS-LH}}_{\chi,\,\text{con-rovib}}$ are based on scaled frequencies, they include some nontorsional anharmonicity and hence technically they could be called quasiharmonic, but they have no multi-structural anharmonicity due to multiple structures and torsional anharmonicity. Note that the partition functions are taken to have their zero of energy at the GM of the reactant (for χ = R) or the transition state (for χ =‡). Rewriting eq 12 with the help of eqs S2 and S3, we have

$$F^{\text{MS-T}}(T) = \frac{Q^{\text{MS-T}}_{\ddagger,\,\text{con-rovib}}(T)\, Q^{\text{SS-HO}}_{\text{R, rovib, GM}}(T)}{Q^{\text{MS-T}}_{\text{R, con-rovib}}(T)\, Q^{\text{SS-HO}}_{\ddagger,\,\text{rovib, GM}}(T)} \tag{S4}$$

For the reverse reaction rates the reactants are the species on the right-hand sides of reactions R1 to R3. In these cases both the product radicals and the H_2O_2 molecule have torsions. Therefore $F^{\text{R}}_{\text{MS-T}}$, $F^{\text{R}}_{\text{MS-LH}}$, and F^{R}_{T} for the reverse reaction all have contributions from both the radical and H_2O_2.

Multi-structural partition functions and anharmonicity factors

The partition functions, Q, and the anharmonicity factors, F, for the reactant, product radicals, and TS were calculated with the M08-HX/maug-cc-pVTZ Hessians from the formatted checkpoint files of all the optimized structures by using the *MSTor* program. The M08-HX/maug-cc-pVTZ density functional frequencies are scaled by a standard scaling factor of 0.976 that accounts for nontorsional anharmonicity and higher-order correlation effects. For the reactant, the product radicals, and the TS, the Voronoi tessellation method was used to calculate the local periodicity parameters, $M_{j,\tau}$, where j labels a structure, and τ labels a torsional coordinate. Two-dimensional Voronoi calculations for butanal, butanoyl radical, 1-oxo-2-butyl radical, and 4-oxo-2-butyl radical and five-dimensional for transition states were used for the calculations of $M_{j,\tau}$, and the results are given in Table S5 and S6.

Since the multi-structural anharmonicity factor ($F^{\chi}_{\text{MS-T}}$) is the product of the multiple-structure factor ($F^{\chi}_{\text{MS-LH}}$) and the torsional anharmonicity factor (F^{χ}_{T}), we tabulated the contributing factors for all the reacting species and the TS in Tables S7–S12. It is clear from those tables that F^{χ}_{T} follows similar trend as that of $F^{\chi}_{\text{MS-T}}$ while the MS-LH factors gradually increase with increase in temperature for each species.

Table S6. Calculated conformational-rotational-vibrational partition function and anharmonicity factors of butanal

T (K)	SS-HO	SS-T	MS-LH	MS-T	$F^{\mathrm{R}}_{\mathrm{MS\text{-}LH}}$	$F^{\mathrm{R}}_{\mathrm{T}}$	$F^{\mathrm{R}}_{\mathrm{MS\text{-}T}}$
200	3.494E–71	3.804E–71	1.465E–70	1.662E–70	4.19	1.13	4.76
250	1.250E–55	1.397E–55	5.929E–55	7.044E–55	4.74	1.19	5.64
298.15	1.778E–45	2.043E–45	9.429E–45	1.170E–44	5.30	1.24	6.58
300	3.775E–45	4.343E–45	2.011E–44	2.500E–44	5.33	1.24	6.62
400	8.427E–32	1.027E–31	5.425E–31	7.279E–31	6.44	1.34	8.64
500	1.585E–23	2.036E–23	1.173E–22	1.661E–22	7.40	1.42	10.48
600	8.592E–18	1.154E–17	7.061E–17	1.033E–16	8.22	1.46	12.02
800	3.722E–10	5.332E–10	3.527E–09	5.263E–09	9.48	1.49	14.14
1000	4.144E–05	6.153E–05	4.304E–04	6.307E–04	10.39	1.47	15.22
1300	7.489E+00	1.130E+01	8.498E+01	1.168E+02	11.35	1.37	15.59
1500	3.307E+03	4.953E+03	3.908E+04	5.078E+04	11.82	1.30	15.35
1800	5.315E+06	7.741E+06	6.566E+07	7.784E+07	12.35	1.19	14.65
2000	3.257E+08	4.620E+08	4.116E+09	4.580E+09	12.64	1.11	14.06
2400	3.313E+11	4.408E+11	4.333E+12	4.247E+12	13.08	0.98	12.82
3000	1.237E+15	1.473E+15	1.675E+16	1.368E+16	13.54	0.82	11.05

Table S7. Calculated conformational-rotational-vibrational partition function and anharmonicity factors of butanoyl radical

T (K)	SS-HO	SS-T	MS-LH	MS-T	$F_{\text{MS-LH}}^{\text{P1}}$	F_{T}^{P1}	$F_{\text{MS-T}}^{\text{P1}}$
200	5.872E–63	6.568E–63	4.866E–62	5.885E–62	8.29	1.21	10.02
250	4.906E–49	5.691E–49	4.417E–48	5.466E–48	9.00	1.24	11.14
298.15	6.152E–40	7.396E–40	5.892E–39	7.404E–39	9.58	1.26	12.04
300	1.209E–39	1.455E–39	1.160E–38	1.459E–38	9.60	1.26	12.07
400	1.160E–27	1.494E–27	1.221E–26	1.563E–26	10.52	1.28	13.47
500	3.226E–20	4.378E–20	3.614E–19	4.646E–19	11.20	1.29	14.40
600	4.765E–15	6.711E–15	5.584E–14	7.129E–14	11.72	1.28	14.96
800	3.798E–08	5.559E–08	4.727E–07	5.811E–07	12.45	1.23	15.30
1000	1.420E–03	2.090E–03	1.837E–02	2.132E–02	12.94	1.16	15.01
1300	8.429E+01	1.214E+02	1.132E+03	1.184E+03	13.42	1.05	14.04
1500	2.144E+04	2.999E+04	2.927E+05	2.845E+05	13.66	0.97	13.27
1800	1.775E+07	2.351E+07	2.472E+08	2.148E+08	13.92	0.87	12.10
2000	7.539E+08	9.576E+08	1.060E+10	8.556E+09	14.06	0.81	11.35
2400	4.150E+11	4.821E+11	5.922E+12	4.149E+12	14.27	0.70	10.00
3000	7.508E+14	7.591E+14	1.088E+16	6.254E+15	14.49	0.57	8.33

Table S8. Calculated conformational-rotational-vibrational partition function and anharmonicity factors of 1-oxo-2-butyl radical[a]

T (K)	SS-HO	SS-T	MS-LH	MS-T	$F_{\mathrm{MS\text{-}LH}}^{\mathrm{P2}}$	$F_{\mathrm{T}}^{\mathrm{P2}}$	$F_{\mathrm{MS\text{-}T}}^{\mathrm{P2}}$
200	4.005E–62	4.900E–62	9.182E–62	1.115E–61	2.29	1.21	2.78
250	2.644E–48	3.339E–48	6.405E–48	8.011E–48	2.42	1.25	3.03
298.15	2.840E–39	3.662E–39	7.221E–39	9.228E–39	2.54	1.28	3.25
300	5.553E–39	7.164E–39	1.414E–38	1.809E–38	2.55	1.28	3.26
400	4.356E–27	5.746E–27	1.207E–26	1.589E–26	2.77	1.32	3.65
500	1.074E–19	1.422E–19	3.183E–19	4.247E–19	2.96	1.33	3.95
600	1.469E–14	1.928E–14	4.587E–14	6.142E–14	3.12	1.34	4.18
800	1.070E–07	1.353E–07	3.608E–07	4.775E–07	3.37	1.32	4.46
1000	3.810E–03	4.580E–03	1.356E–02	1.747E–02	3.56	1.29	4.59
1300	2.180E+02	2.404E+02	8.181E+02	9.979E+02	3.75	1.22	4.58
1500	5.463E+04	5.674E+04	2.104E+05	2.459E+05	3.85	1.17	4.50
1800	4.463E+07	4.231E+07	1.770E+08	1.930E+08	3.97	1.09	4.32
2000	1.884E+09	1.680E+09	7.586E+09	7.879E+09	4.03	1.04	4.18
2400	1.029E+12	8.143E+11	4.242E+12	3.989E+12	4.12	0.94	3.88
3000	1.849E+15	1.233E+15	7.812E+15	6.329E+15	4.23	0.81	3.42

[a] The zero of energy is at the lowest-energy classical equilibrium structure

Table S9. Calculated conformational-rotational-vibrational partition function and anharmonicity factors of 4-oxo-2-butyl radical[a]

T (K)	SS-HO	SS-T	MS-LH	MS-T	$F_{\text{MS-LH}}^{\text{P3}}$	F_{T}^{P3}	$F_{\text{MS-T}}^{\text{P3}}$
200	4.012E–60	5.536E–60	5.669E–60	7.715E–60	1.41	1.36	1.92
250	1.440E–46	2.025E–46	2.342E–46	3.256E–46	1.63	1.39	2.26
298.15	1.073E–37	1.513E–37	1.955E–37	2.742E–37	1.82	1.40	2.56
300	2.074E–37	2.925E–37	3.795E–37	5.321E–37	1.83	1.40	2.57
400	1.059E–25	1.456E–25	2.319E–25	3.211E–25	2.19	1.38	3.03
500	2.078E–18	2.713E–18	5.157E–18	6.876E–18	2.48	1.33	3.31
600	2.473E–13	3.024E–13	6.725E–13	8.514E–13	2.72	1.27	3.44
800	1.544E–06	1.624E–06	4.742E–06	5.316E–06	3.07	1.12	3.44
1000	5.075E–02	4.567E–02	1.684E–01	1.661E–01	3.32	0.99	3.27
1300	2.718E+03	1.954E+03	9.702E+03	7.940E+03	3.57	0.82	2.92
1500	6.644E+05	4.154E+05	2.451E+06	1.783E+06	3.69	0.73	2.68
1800	5.298E+08	2.729E+08	2.026E+09	1.250E+09	3.82	0.62	2.36
2000	2.212E+10	1.011E+10	8.612E+10	4.794E+10	3.89	0.56	2.17
2400	1.191E+13	4.379E+12	4.763E+13	2.193E+13	4.00	0.46	1.84
3000	2.114E+16	5.856E+15	8.688E+16	3.114E+16	4.11	0.36	1.47

[a] The zero of energy is at the lowest-energy classical equilibrium structure

Table S10. Calculated conformational-rotational-vibrational partition function and anharmonicity factors of H_2O_2[a]

T (K)	SS-HO	SS-T	MS-LH	MS-T	$F_{\text{MS-LH}}^{\text{H}_2\text{O}_2}$	$F_{\text{T}}^{\text{H}_2\text{O}_2}$	$F_{\text{MS-T}}^{\text{H}_2\text{O}_2}$
200	5.078E–16	5.287E–16	1.016E–15	1.058E–15	2.00	1.04	2.08
250	3.454E–12	3.645E–12	6.908E–12	7.291E–12	2.00	1.055	2.11
298.15	1.112E–09	1.190E–09	2.224E–09	2.380E–09	2.00	1.07	2.14
300	1.340E–09	1.434E–09	2.679E–09	2.869E–09	2.00	1.07	2.14
400	2.698E–06	2.972E–06	5.396E–06	5.945E–06	2.00	1.10	2.20
500	3.022E–04	3.410E–04	6.044E–04	6.820E–04	2.00	1.13	2.26
600	7.900E–03	9.080E–03	1.580E–02	1.815E–02	2.00	1.15	2.30
800	5.941E–01	6.955E–01	1.188E+00	1.391E+00	2.00	1.17	2.34
1000	9.971E+00	1.170E+01	1.994E+01	2.340E+01	2.00	1.175	2.35
1300	1.792E+02	2.075E+02	3.585E+02	4.151E+02	2.00	1.16	2.32
1500	7.489E+02	8.541E+02	1.498E+03	1.708E+03	2.00	1.14	2.28
1800	4.143E+03	4.597E+03	8.286E+03	9.194E+03	2.00	1.11	2.22
2000	1.064E+04	1.157E+04	2.128E+04	2.315E+04	2.00	1.09	2.18
2400	5.120E+04	5.350E+04	1.024E+05	1.070E+05	2.00	1.045	2.09
3000	3.239E+05	3.190E+05	6.478E+05	6.380E+05	2.00	0.985	1.97

[a] The zero of energy is at the lowest-energy classical equilibrium structure

For H_2O_2, we obtain two structures which are mirror images and hence distinguishable. Therefore, in the case of H_2O_2, the local periodicity parameter $M_{j,\tau}$ is 2.

Table S11. Calculated conformational-rotational-vibrational partition function and anharmonicity factors of the transition states[a]

T (K)	SS-HO	SS-T	MS-LH	MS-T	$F^{\ddagger}_{\text{MS-LH}}$	$F^{\ddagger}_{\text{T}}$	$F^{\ddagger}_{\text{MS-T}}$
transition stateleading to the formation of butanoyl radical (R1)							
200	4.11E-77	4.78E-77	9.18E-76	1.19E-75	22.35	1.30	28.97
250	1.12E-59	1.36E-59	3.23E-58	4.56E-58	28.97	1.41	40.84
298.15	3.04E-48	3.89E-48	1.06E-46	1.61E-46	34.98	1.52	53.15
300	7.11E-48	9.13E-48	2.50E-46	3.81E-46	35.20	1.52	53.63
400	9.87E-33	1.40E-32	4.56E-31	7.87E-31	46.22	1.73	79.81
500	2.97E-23	4.63E-23	1.64E-21	3.09E-21	55.37	1.88	104.19
600	1.26E-16	2.13E-16	7.93E-15	1.57E-14	62.96	1.99	125.07
800	1.06E-07	2.03E-07	7.94E-06	1.65E-05	74.61	2.07	154.70
1000	1.00E-01	2.05E-01	8.33E+00	1.70E+01	83.04	2.05	169.82
1300	1.96E+05	4.15E+05	1.80E+07	3.40E+07	91.98	1.89	173.59
1500	3.03E+08	6.37E+08	2.92E+10	5.10E+10	96.36	1.75	168.51
1800	2.32E+12	4.68E+12	2.36E+14	3.61E+14	101.41	1.53	155.37
2000	3.47E+14	6.68E+14	3.61E+16	5.03E+16	104.07	1.39	145.01
2400	1.61E+18	2.79E+18	1.75E+20	2.00E+20	108.23	1.15	123.97
3000	3.79E+22	5.41E+22	4.26E+24	3.64E+24	112.61	0.85	96.11
transition state leading to the formation of 1-oxo-2-butyl radical (R2)							
200	1.51E-77	1.65E-77	5.62E-77	6.17E-77	3.72	1.10	4.08
250	3.35E-60	3.74E-60	1.95E-59	2.22E-59	5.83	1.14	6.63
298.15	7.95E-49	9.10E-49	7.08E-48	8.33E-48	8.90	1.18	10.48
300	1.85E-48	2.12E-48	1.68E-47	1.97E-47	9.04	1.18	10.65
400	2.14E-33	2.58E-33	4.02E-32	5.04E-32	18.82	1.25	23.58
500	5.73E-24	7.30E-24	1.85E-22	2.43E-22	32.33	1.31	42.50
600	2.25E-17	3.02E-17	1.09E-15	1.49E-15	48.28	1.36	65.89
800	1.74E-08	2.55E-08	1.45E-06	2.08E-06	83.16	1.44	119.42
1000	1.56E-02	2.47E-02	1.84E+00	2.70E+00	117.68	1.47	173.22
1300	2.92E+04	5.09E+04	4.80E+06	7.04E+06	164.25	1.47	241.23
1500	4.44E+07	8.15E+07	8.49E+09	1.22E+10	191.18	1.44	274.84
1800	3.35E+11	6.51E+11	7.58E+13	1.03E+14	225.90	1.36	307.85
2000	4.97E+13	9.88E+13	1.22E+16	1.59E+16	245.77	1.30	319.94
2400	2.29E+17	4.68E+17	6.40E+19	7.48E+19	279.21	1.17	326.38
3000	5.33E+21	1.08E+22	1.69E+24	1.65E+24	317.55	0.97	309.02

transition stateleading to the formation of 4-oxo-2-butyl radical (R3)

200	4.10E-77	4.47E-77	2.60E-76	2.84E-76	6.35	1.09	6.93
250	7.40E-60	8.27E-60	6.16E-59	7.02E-59	8.32	1.14	9.48
298.15	1.54E-48	1.77E-48	1.70E-47	2.05E-47	11.00	1.21	13.29
300	3.58E-48	4.12E-48	3.99E-47	4.83E-47	11.13	1.21	13.47
400	3.53E-33	4.30E-33	7.40E-32	1.03E-31	20.98	1.39	29.18
500	8.67E-24	1.12E-23	3.32E-22	5.13E-22	38.30	1.55	59.19
600	3.24E-17	4.38E-17	2.05E-15	3.37E-15	63.37	1.64	104.15
800	2.35E-08	3.43E-08	3.10E-06	5.28E-06	131.74	1.70	224.50
1000	2.04E-02	3.12E-02	4.36E+00	7.21E+00	213.78	1.65	353.45
1300	3.72E+04	5.91E+04	1.27E+07	1.89E+07	342.24	1.48	507.51
1500	5.61E+07	9.00E+07	2.38E+10	3.21E+10	424.43	1.35	572.43
1800	4.19E+11	6.74E+11	2.26E+14	2.60E+14	537.81	1.15	619.29
2000	6.19E+13	9.89E+13	3.75E+16	3.87E+16	606.17	1.03	625.17
2400	2.84E+17	4.45E+17	2.06E+20	1.70E+20	726.35	0.83	599.79
3000	6.57E+21	9.87E+21	5.73E+24	3.42E+24	871.70	0.60	520.83

transition stateleading to the formation of 4-oxo-1-butyl radical (R4)

200	5.71E-77	5.87E-77	1.38E-76	1.44E-76	2.42	1.04	2.52
250	1.11E-59	1.15E-59	3.16E-59	3.42E-59	2.84	1.08	3.07
298.15	2.41E-48	2.51E-48	8.50E-48	9.77E-48	3.53	1.15	4.05
300	5.60E-48	5.84E-48	2.00E-47	2.30E-47	3.56	1.15	4.10
400	5.69E-33	6.03E-33	3.78E-32	4.98E-32	6.65	1.32	8.76
500	1.41E-23	1.52E-23	1.83E-22	2.59E-22	12.97	1.41	18.33
600	5.29E-17	5.79E-17	1.22E-15	1.76E-15	23.14	1.44	33.26
800	3.86E-08	4.37E-08	2.09E-06	2.88E-06	54.07	1.38	74.72
1000	3.36E-02	3.95E-02	3.18E+00	4.05E+00	94.82	1.27	120.78
1300	6.13E+04	7.67E+04	1.00E+07	1.09E+07	163.58	1.09	178.35
1500	9.24E+07	1.20E+08	1.94E+10	1.89E+10	209.88	0.97	204.19
1800	6.91E+11	9.55E+11	1.91E+14	1.56E+14	276.02	0.82	225.21
2000	1.02E+14	1.46E+14	3.23E+16	2.34E+16	316.96	0.73	229.97
2400	4.68E+17	7.15E+17	1.83E+20	1.05E+20	390.67	0.58	225.25
3000	1.08E+22	1.80E+22	5.22E+24	2.18E+24	482.27	0.42	201.02

[a] The zero of energy is at the lowest-energy classical equilibrium structure and single-structure (SS) results are for global minimum structure.

Table S12. The SCT transmission coefficients for the reactions R1 – R3.

T(K)	$\kappa_{\mathrm{R1}}^{\mathrm{SCT}}$	$\kappa_{\mathrm{R2}}^{\mathrm{SCT}}$	$\kappa_{\mathrm{R3}}^{\mathrm{SCT}}$
200	8.13E+03	1.92E+06	3.23E+02
250	4.01E+02	1.78E+04	5.32E+01
300	6.62E+01	1.13E+03	1.80E+01
400	1.01E+01	5.97E+01	5.55E+00
500	4.26E+00	1.41E+01	3.09E+00
600	2.69E+00	6.28E+00	2.22E+00
800	1.73E+00	2.79E+00	1.58E+00
1000	1.41E+00	1.92E+00	1.34E+00
1300	1.23E+00	1.47E+00	1.19E+00
1500	1.16E+00	1.33E+00	1.14E+00
1800	1.11E+00	1.22E+00	1.10E+00
2000	1.09E+00	1.17E+00	1.08E+00
2400	1.06E+00	1.12E+00	1.05E+00

Table S13. Reaction rate constants (cm^3 molecule^{-1} s^{-1}) based on the multi-structural conventional transition state theory (MS-TST)[a]

T(K)	R1	R2	R3	R4
200	3.60E-25	5.34E-32	3.98E-32	2.51E-34
250	1.00E-22	1.80E-28	1.32E-28	1.93E-30
298.15	4.13E-21	4.08E-26	2.96E-26	7.45E-28
300	4.66E-21	4.87E-26	3.53E-26	9.05E-28
400	6.80E-19	7.36E-23	6.05E-23	3.27E-24
500	1.60E-17	7.62E-21	7.76E-21	6.78E-22
600	1.47E-16	1.97E-19	2.44E-19	2.95E-20
800	2.93E-15	1.52E-17	2.45E-17	4.47E-18
1000	2.10E-14	2.59E-16	4.80E-16	1.12E-16
1300	1.55E-13	4.50E-15	9.13E-15	2.69E-15
1500	4.07E-13	1.78E-14	3.66E-14	1.20E-14
1800	1.25E-12	8.65E-14	1.78E-13	6.54E-14
2000	2.27E-12	2.00E-13	4.06E-13	1.59E-13
2400	5.86E-12	7.57E-13	1.48E-12	6.35E-13

[a] without tunneling or variational effects

Table S14. Multi-structural CVT/SCT rate constants (in cm^3 molecule^{-1} s^{-1}) for the reverse reactions as a function of temperature

T(K)	–R1	–R2	–R3
200	1.37E-18	2.84E-22	2.79E-18
250	3.45E-18	1.30E-21	4.21E-18
298.15	8.40E-18	5.90E-21	7.14E-18
300	8.69E-18	6.25E-21	7.30E-18
400	4.79E-17	1.00E-19	2.63E-17
500	2.02E-16	9.18E-19	9.09E-17
600	6.65E-16	5.38E-18	2.70E-16
800	4.12E-15	7.65E-17	1.48E-15
1000	1.57E-14	5.16E-16	5.23E-15
1300	6.87E-14	4.07E-15	2.12E-14
1500	1.49E-13	1.15E-14	4.33E-14
1800	3.67E-13	3.95E-14	1.03E-13
2000	5.99E-13	7.74E-14	1.65E-13
2400	1.34E-12	2.30E-13	3.60E-13

Details of the MCMM reaction path used in Figures 2a, 2b, and 2c

The minimum energy paths (MEPs) through the GM TSs for the three reactions R1, R2, and R3 were obtained with multiconfiguration Shepard interpolation (MCSI) and MC-TINKERATE programs. For the placement of the Shepard points, we followed the strategy developed in the work of Albu *et al.*[58], but slightly modified here. The details of the reaction paths are given below. The MCSI procedure results in a V_{MEP} profile that is well converged, and so we used MCSI for the potential energy V_{MEP} along each MEP. Note that MCSI was originally called MCMM, but we changed the name to emphasis the interpolation aspect. The rate constants were calculated using the MC-TINKERATE program in conjunction with the POLYRATE program.

The Shepard points for R1 in Figure S1 were placed at

1. s = 0.0 Å (saddle point geometry).
2. s = 0.119 Å (one quarter down from the saddle point along the MCMM-0 reaction path on the dynamical bottleneck side).
3. s = -0.214 Å (one quarter down from the saddle point along the MCMM-1 reaction path on the side opposite to the dynamical bottleneck side).
4. s = 0.167 Å (one half down from the saddle point along the MCMM-2 reaction path on the dynamical bottleneck side).
5. s = 0.254 Å (lower than the saddle point by three-fourth of the average of forward and reverse barrier heights along MCMM-3 reaction path on the dynamical bottleneck side).
6. s = 0.085 Å (one-eighth down from the saddle point along the MCMM-4 reaction path on the dynamical bottleneck side).

7. *s* = –0.108 Å (one-eighth down from the saddle point along the MCMM-5 reaction path on the side opposite to the dynamical bottleneck side).
8. *s* = -0.312 Å (additional point on MCMM-6 reaction path on the side opposite to the dynamical bottleneck side).
9. *s* = 0.405 Å (additional point on MCMM-7 reaction path on the dynamical bottleneck side).
10. *s* = -0.945 Å (additional point on MCMM-7 reaction path on the side opposite to the dynamical bottleneck side).
11. *s* = 0.405 Å (additional point on MCMM-9 reaction path on the dynamical bottleneck side).
12. *s* = 0.675 Å (additional point on MCMM-9 reaction path on the dynamical bottleneck side).

The Shepard points for R2 in Figure S1 were placed at

1. *s* = 0.0 Å (saddle point geometry).
2. *s* = 0.156 Å (one quarter down from the saddle point along the MCMM-0 reaction path on the dynamical bottleneck side).
3. *s* = -0.137 Å (one quarter down from the saddle point along the MCMM-1 reaction path on the side opposite to the dynamical bottleneck side).
4. *s* = 0.299 Å (one half down from the saddle point along the MCMM-2 reaction path on the dynamical bottleneck side).
5. *s* = -0.233 Å (one half down from the saddle point along the MCMM-3 reaction path on the side opposite to the dynamical bottleneck side).

6. s = 0.553 Å (lower than the saddle point by three-fourth of the average of forward and reverse barrier heights along MCMM-4 reaction path on the dynamical bottleneck side).
7. s = 0.100 Å (one-eighth down from the saddle point along the MCMM-5 reaction path on the dynamical bottleneck side).
8. s = -0.450 Å (three-fourth down from the saddle point along the MCMM-6 reaction path on the side opposite to the dynamical bottleneck side).

The Shepard points for R3 in Figure S1 were placed at

1. s = 0.0 Å (saddle point geometry).
2. s = 0.074 Å (one quarter down from the saddle point along the MCMM-0 reaction path on the dynamical bottleneck side).
3. s = -0.082 Å (one quarter down from the saddle point along the MCMM-1 reaction path on the side opposite to the dynamical bottleneck side).
4. s = 0.119 Å (one half down from the saddle point along the MCMM-2 reaction path on the dynamical bottleneck side).
5. s = -0.127 Å (one half down from the saddle point along the MCMM-3 reaction path on the side opposite to the dynamical bottleneck side).
6. s = 0.394 Å (lower than the saddle point by three-fourth of the average of forward and reverse barrier heights along MCMM-4 reaction path on the dynamical bottleneck side).
7. s = 0.055 Å (one-eighth down from the saddle point along the MCMM-5 reaction path on the dynamical bottleneck side).
8. s = -0.198 Å (three-fourth down from the saddle point along the MCMM-6 reaction path on the side opposite to the dynamical bottleneck side).

Internal coordinates

Non-redundant internal coordinates are used to calculate generalized normal mode frequencies along the reaction paths and/or used in the MS-T calculations. The internal coordinates are listed below. Note that *i-j* denote bond between atom *i* and *j*; *i-j-k* denotes bond angle formed by atoms *i*, *j*, and *k*; i-j-k-l denotes torsion angle or improper torsion angle formed by atoms *i*, *j*, *k*, and *l*;

R1: (see Fig. 1(b) for atomic numbering)

1-5 1-8 8-6 6-7 7-9 1-2 2-10 2-11
2-3 3-12 3-13 3-4 4-14 4-15 4-16 5-1-8
1-8-6 5-1-2 8-1-2 8-6-7 6-7-9 10-2-11 1-2-10 1-2-11
10-2-3 11-2-3 2-3-12 2-3-13 12-3-13 12-3-4 13-3-4 3-4-14
3-4-16 14-4-15 14-4-16 15-4-16 5-1-2-3 1-2-3-4 2-3-4-15 5-1-8-6
1-8-6-7 8-6-7-9

R2: (see Fig. 1(d) for atomic numbering)

1-5 1-16 1-2 2-10 2-9 9-6 6-7 7-8
2-3 3-11 3-12 3-4 4-13 4-14 4-15 5-1-16
5-1-2 16-5-1-2 1-2-10 1-2-9 9-2-10 9-2-3 10-2-3 2-9-6
9-6-7 6-7-8 2-3-11 2-3-12 11-3-12 11-3-4 12-3-4 3-4-14
3-4-15 13-4-14 13-4-15 14-4-15 5-1-2-3 1-2-3-4 2-3-4-13 10-2-9-6
2-9-6-7 9-6-7-8

R3: (see Fig. 1(f) for atomic numbering)

1-2 1-5 1-16 2-9 2-10 2-3 3-11 3-12
3-4 11-6 6-7 7-8 4-13 4-14 4-15 16-1-5
5-1-2 16-1-2 1-2-9 1-2-10 9-2-10 9-2-3 10-2-3 2-3-1
2-3-12 11-3-12 11-3-4 12-3-4 3-11-6 11-6-7 6-7-8 3-4-14

3-4-15 14-4-15 13-4-14 13-4-15 5-1-2-3 1-2-3-4 2-3-4-13 12-3-11-6
3-11-6-7 11-6-7-8

R4: (see Fig. 1(h) for atomic numbering)

1-2 1-3 1-4 1-5 2-14 14-15 15-16 5-6
5-7 5-8 8-9 8-10 8-11 11-12 11-13 16-15-14
15-14-2 14-2-1 2-1-3 3-1-4 3-1-5 4-1-5 2-1-5 1-5-6
1-5-7 6-5-7 6-5-8 7-5-8 5-8-9 5-8-10 9-8-10 9-8-11
10-8-11 8-11-12 8-11-13 8-12-13-11 13-11-8-5 11-8-5-1 8-5-1-2 5-1-2-14
1-2-14-15 2-14-15-16

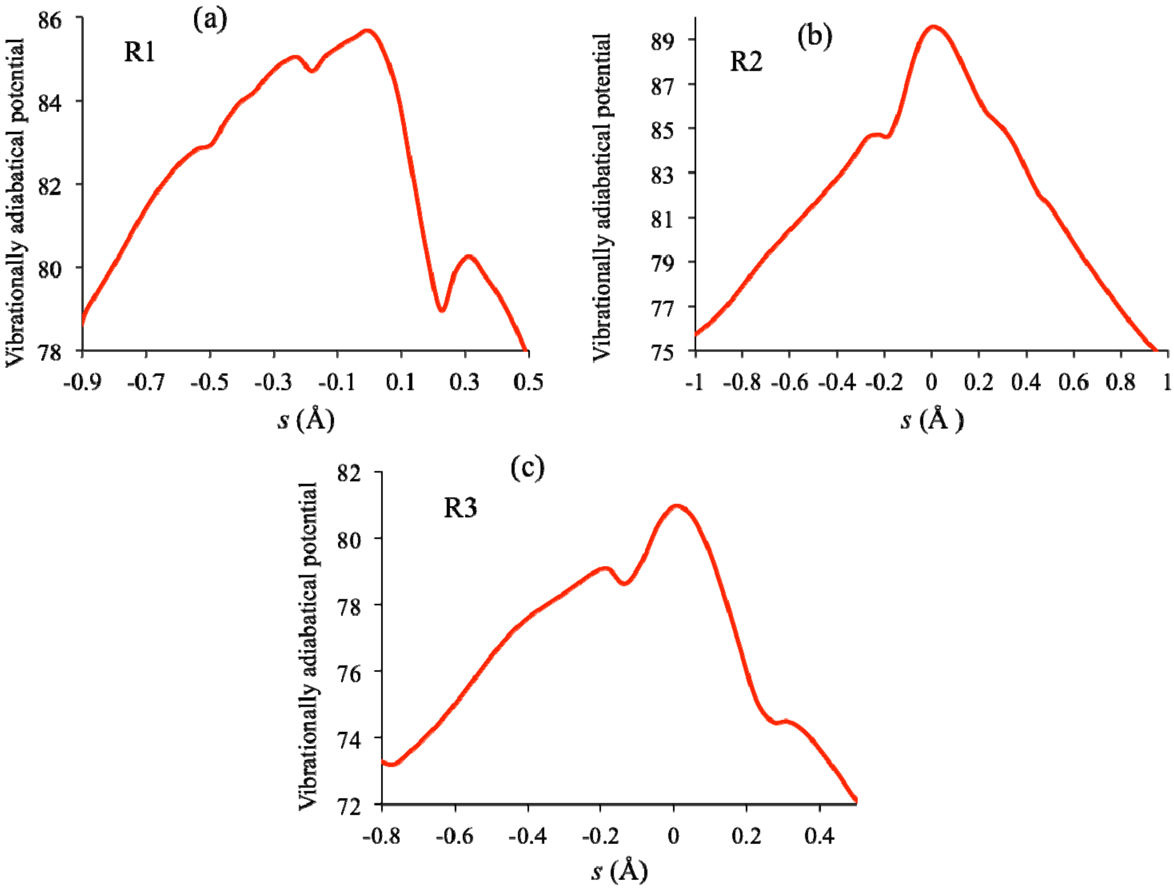

Figure S1. Calculated $V_{\mathrm{a}}^{\mathrm{G}}$ (kcal/mol) as a function of the reaction coordinate, *s*, scaled to a reduced mass of 1 amu, for hydrogen abstraction from (a) the carbonyl-C of butanal by •O_2H to form butanoyl radical, (b) the *α*-C of butanal by •O_2H to form 1-oxo-2-butyl radical, and (c) the *β*-C of butanal by •O_2H to form 4-oxo-2-butyl radical. The zero of energy for these figures and for the representative tunneling energies in table 3 is the potential energy of the equilibrium structure of infinitely separately reactants, i.e., the global minimum (GM) of reactants.