Autoxidation of Ethylbenzene: the Mechanism Elucidated

Ive Hermans[a*], *Jozef Peeters*[b], *Pierre A. Jacobs*[a]

a Centre for Surface Chemistry and Catalysis, Department of Microbial and Molecular Systems (M^2S), K.U.Leuven

Kasteelpark Arenberg 23, B-3001 Heverlee, Belgium

Tel (+32) 16 321648 Fax (+32) 16 321998

b Division for Quantum Chemistry and Physical Chemistry, Department of Chemistry, K.U.Leuven

Celestijnenlaan 200F, B-3001 Heverlee, Belgium

AUTHOR EMAIL ADDRESS ive.hermans@biw.kuleuven.be

SUPPORTING INFORMATION

TS for $CH_3OO^{\bullet} + RH \rightarrow CH_3OOH + R^{\bullet}$

E(UB+HF-LYP/6-31G(d,p)) (Hartree): -501.081294914
Electronic state : 2-A
Cartesian coordinates (Angs):

C	1.366644	2.471911	-0.344603
C	0.792919	1.430445	0.597681
H	0.692982	3.333907	-0.440745
H	1.537587	2.068164	-1.346745
H	2.328020	2.835835	0.027793
H	1.707810	0.468609	0.533564
O	2.593449	-0.349036	0.349493
O	2.061915	-1.215730	-0.612013
C	1.541819	-2.363868	0.057145
H	2.329188	-2.865379	0.629719
H	0.713045	-2.091705	0.719048
H	1.180298	-3.020886	-0.739072
H	0.860768	1.713920	1.652105
C	-0.470262	0.751087	0.274021
C	-1.276547	0.234564	1.312918
H	-0.965347	0.383961	2.344023
C	-2.457747	-0.446573	1.038535
H	-3.065087	-0.825667	1.855734
C	-0.896612	0.541400	-1.055011
H	-0.294938	0.914505	-1.876829
C	-2.867286	-0.636992	-0.285731
H	-3.790367	-1.166962	-0.501717
C	-2.080598	-0.139548	-1.327920
H	-2.390850	-0.284734	-2.358917

Rotational constants (GHz): 1.3692000 0.7798200 0.6317400
Vibrational harmonic frequencies (cm-1):

-1715.5935	23.7107	38.2199
49.0160	110.0638	123.1680
154.7984	171.2110	212.4313
230.3832	327.9681	412.7943
416.0625	463.7781	507.1932
542.9178	583.5088	630.6358
702.7768	772.7624	792.0853
848.6401	857.7211	920.5547
940.5221	971.8068	996.3095
1007.2395	1015.3568	1055.7788
1059.8691	1071.0579	1114.6043
1136.5160	1162.2976	1169.3135
1185.8463	1206.0460	1213.3870
1239.9895	1332.2459	1363.4410
1395.3717	1424.3288	1457.8256
1475.9314	1481.2413	1494.2799

1501.1937	1507.6411	1511.9645
1532.6553	1619.8300	1642.2820
3031.8614	3036.3830	3095.8536
3104.9942	3116.1512	3133.0167
3137.9541	3175.6651	3184.9804
3194.3330	3206.5264	3216.3482

Zero-point correction (Hartree): 0.195496

TS for $CH_3OO^{\bullet}$ + ROOH → CH_3OOH + $R_{-\alpha H}{}^{\bullet}OOH$

E(UB+HF-LYP/6-31G(d,p)) (Hartree): -651.428543252
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-0.604841	-0.501904	2.167559
C	-0.359716	0.045485	0.769021
H	-0.069530	0.102501	2.909043
H	-0.238110	-1.528435	2.238107
H	-1.670553	-0.491137	2.409472
H	-1.078829	-0.696560	-0.025896
O	-1.912178	-1.262953	-0.776189
O	-2.809334	-0.232486	-1.124223
C	-3.949832	-0.309081	-0.266934
H	-4.408417	-1.299289	-0.339041
H	-3.676160	-0.091838	0.770488
H	-4.640236	0.454247	-0.636893
C	1.047334	-0.034176	0.265214
C	1.617077	-1.292588	0.012668
H	1.015284	-2.189828	0.133467
C	2.941054	-1.400876	-0.407041
H	3.367397	-2.380873	-0.600782
C	1.826861	1.117651	0.073113
H	1.389189	2.092028	0.254850
C	3.713683	-0.250871	-0.585911
H	4.745404	-0.332773	-0.915479
C	3.151654	1.005017	-0.344401
H	3.747742	1.902642	-0.482790
O	-0.987211	1.293054	0.707695
O	-0.929011	1.811353	-0.653841
H	-1.680960	1.315635	-1.041819

Rotational constants (GHz): 1.4559000 0.4458300 0.4209800
Vibrational harmonic frequencies (cm-1):

-1559.7157	46.3492	52.0366
58.9983	104.0046	122.4390
145.5397	173.6180	185.3574

215.7269	236.2422	254.0199
258.4703	315.1249	409.7565
413.0515	463.3899	483.2195
494.3710	572.2653	594.8106
630.2201	669.3154	708.1915
767.8968	794.1238	856.9187
894.6856	924.0717	929.1628
961.7190	975.2594	999.1794
1014.5222	1035.2665	1051.7855
1059.3208	1108.3156	1115.0889
1153.6689	1173.7984	1187.3180
1188.5589	1209.4667	1213.7440
1300.2820	1341.8571	1363.8898
1410.8263	1451.4839	1463.8824
1481.9224	1485.9635	1487.2390
1499.6840	1511.3376	1533.4467
1553.8640	1630.8732	1650.9996
3043.8644	3049.5865	3124.1812
3128.9284	3143.8973	3150.3205
3178.4003	3186.2120	3196.6682
3208.5162	3232.5877	3584.4524

Zero-point correction (Hartree): 0.204159

$(CH_3)_2C(O^{\bullet})H + RH \rightarrow (CH_3)_2C(OH)H + R^{\bullet}$

E(UB+HF-LYP/6-31G(d,p)) (Hartree): -504.576988079
Electronic state : 2-A
Cartesian coordinates (Angs):

C	0.017916	1.264419	-0.676990
H	0.971921	0.830458	-0.053168
H	0.310625	1.076485	-1.715997
C	0.033448	2.753601	-0.353996
H	0.995696	3.188925	-0.635846
H	-0.758502	3.283101	-0.897919
H	-0.109797	2.943111	0.713585
O	2.178005	0.576595	0.511029
C	2.795396	-0.497210	-0.148357
H	2.801968	-0.322087	-1.239813
C	4.261343	-0.481475	0.325416
H	4.309140	-0.642064	1.406859
H	4.825036	-1.277798	-0.171806
H	4.727124	0.480275	0.096473
C	2.111742	-1.837104	0.145320
H	1.067798	-1.820791	-0.182257

H	2.617444	-2.662754	-0.368312
H	2.123784	-2.036541	1.221933
C	-1.183885	0.467191	-0.308407
C	-1.912566	0.711715	0.870802
H	-1.609161	1.515307	1.534534
C	-1.602366	-0.594706	-1.132933
H	-1.055291	-0.798068	-2.050444
C	-3.018797	-0.066902	1.203766
H	-3.567366	0.141492	2.118100
C	-2.708252	-1.374634	-0.801164
H	-3.015709	-2.183169	-1.458444
C	-3.422815	-1.113208	0.370299
H	-4.285738	-1.718760	0.631756

Rotational constants (GHz): 1.4011000 0.4631900 0.3967400

Vibrational harmonic frequencies (cm-1):

-967.5788	21.0894	28.1607
45.4813	74.2583	92.8928
158.9163	172.8786	222.0339
232.5007	254.3374	268.1176
339.6718	388.6764	414.4014
420.1003	469.8018	505.0416
553.7211	632.3282	675.1751
707.5847	765.8731	791.8658
829.9158	854.3622	867.6022
924.5567	928.0896	944.3290
970.6641	973.2313	997.9994
1012.1086	1019.5271	1059.0667
1070.1644	1106.3681	1127.7742
1134.4270	1160.2604	1182.5411
1186.7410	1209.6933	1230.3108
1295.4000	1327.1435	1337.9067
1363.8399	1381.3829	1396.2446
1401.9467	1414.9788	1420.9084
1422.4465	1489.6467	1494.7814
1499.1985	1500.3741	1505.8227
1510.8368	1523.4250	1537.4502
1628.4673	1651.3989	2945.2469
3042.2260	3042.7110	3050.5133
3073.4401	3113.8950	3114.6288
3125.5908	3127.6379	3135.9558
3140.3520	3174.0637	3183.2806
3192.9855	3203.1282	3210.3916

Zero-point correction (Hartree): 0.248330

RO•

E(UB+HF-LYP/6-31G(d,p)) (Hartree): -385.430093621
Electronic state : 2-A
Cartesian coordinates (Angs):

C	2.021537	-1.120601	-0.160911
C	0.640596	-1.216267	-0.339662
C	-0.173172	-0.086721	-0.200936
C	0.412396	1.144487	0.108808
C	1.793049	1.241761	0.287082
C	2.600844	0.110024	0.154993
H	2.644154	-2.003755	-0.273827
H	0.193998	-2.175613	-0.594358
H	-0.222893	2.020623	0.191783
H	2.239840	2.203373	0.524251
H	3.675776	0.187443	0.291036
C	-1.683627	-0.207062	-0.367898
H	-1.923616	-1.004188	-1.096962
C	-2.366438	-0.640260	0.976462
H	-2.173811	0.111692	1.744522
H	-3.443121	-0.751287	0.832691
H	-1.933546	-1.592848	1.291391
O	-2.315987	0.956549	-0.707271

Rotational constants (GHz): 3.5806900 1.1348400 0.9671400
Vibrational harmonic frequencies (cm-1):

44.0864	130.9735	202.5691
249.1595	295.7470	360.5254
415.0695	438.7796	537.5283
602.0444	632.6357	716.2898
762.4624	773.9681	865.1145
894.4431	921.8758	933.0018
977.4747	1001.4207	1015.6860
1044.7615	1053.2434	1097.6738
1110.6406	1185.6953	1196.9615
1209.8818	1241.5786	1307.3565
1359.9222	1374.7516	1389.1503
1483.5648	1494.5091	1507.4897
1536.6237	1643.7179	1659.4397
2935.9225	3065.0850	3155.4898
3162.3164	3164.6353	3181.8999
3192.1825	3204.5618	3213.1728

Zero-point correction (Hartree): 0.147951

TS for Ph-CH(O•)-CH_3 → PhCHO + •CH_3

E(UB+HF-LYP/6-31G(d,p)) (Hartree): -385.407508881
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-1.816054	-1.188428	0.415676
C	-0.448649	-1.173556	0.151516
C	0.166370	0.000682	-0.302585
C	-0.603565	1.154165	-0.497083
C	-1.973101	1.139020	-0.234426
C	-2.580248	-0.032399	0.225100
H	-2.291072	-2.100690	0.765528
H	0.163872	-2.060812	0.278384
H	-0.127152	2.062754	-0.860301
H	-2.566633	2.035436	-0.389704
H	-3.646978	-0.046284	0.430025
C	1.633296	0.003287	-0.611135
H	1.979443	0.910445	-1.150664
C	2.388534	0.877059	1.189890
H	2.073029	0.121232	1.899661
H	3.444159	0.899987	0.944572
H	1.864780	1.826694	1.222893
O	2.313383	-1.040968	-0.645265

Rotational constants (GHz): 3.1922700 1.1144500 0.9675000
Vibrational harmonic frequencies (cm-1):

-412.7313	68.4873	109.1278
136.2539	207.3107	229.9718
348.6835	418.2003	435.2335
509.5549	596.7149	608.8793
630.7195	670.6623	709.5659
771.2400	833.0244	866.5297
918.6976	944.0212	982.9542
1006.3941	1015.8950	1028.4207
1049.1856	1103.0250	1185.3559
1188.1993	1215.8979	1332.7185
1362.2688	1387.4237	1429.5563
1442.2658	1486.5413	1531.5049
1570.6177	1645.0447	1655.3856
2898.8455	3116.7769	3167.7145
3184.0082	3194.6151	3206.1936
3214.3114	3281.9199	3290.1509

Zero-point correction (Hartree): 0.143948

TS for Ph-CH(O•)-CH_3 → Ph• + CH(=O)CH_3

E(UB+HF-LYP/6-31G(d,p)) (Hartree): -385.392929446
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-2.091750	1.190478	-0.132229
C	-0.697584	1.236817	-0.293229
C	-0.024706	0.040385	-0.166930
C	-0.596476	-1.186604	0.088147
C	-1.990090	-1.205355	0.245723
C	-2.728713	-0.023668	0.136269
H	-2.671183	2.105827	-0.220258
H	-0.191713	2.173740	-0.506976
H	0.008548	-2.083618	0.160583
H	-2.493184	-2.146397	0.452379
H	-3.807505	-0.048964	0.258381
C	2.178989	-0.037617	-0.404180
H	1.986124	0.377366	-1.417235
C	2.611961	0.977367	0.639061
H	2.498930	0.559801	1.641855
H	3.675707	1.196031	0.476553
H	2.063153	1.919151	0.559671
O	2.370168	-1.250470	-0.260093

Rotational constants (GHz): 3.4594600 1.0083900 0.8225200
Vibrational harmonic frequencies (cm-1):

-244.4562	22.7625	85.9958
125.7102	160.7878	211.1279
296.2185	408.6129	440.6630
494.6366	584.3077	603.4253
673.0155	733.8699	808.1747
822.6420	887.7605	903.3242
960.1322	963.5719	992.9687
1019.5303	1044.5799	1071.7466
1082.9987	1119.6866	1180.5840
1182.1919	1313.8034	1342.5510
1381.2172	1406.6720	1476.2927
1477.9205	1486.2772	1487.5064
1590.8588	1644.3386	1648.2765
2893.3858	3041.5275	3116.2536
3159.4238	3179.3202	3186.8304
3198.2548	3207.6877	3224.6910

Zero-point correction (Hartree): 0.144309

TS reaction (15)

E(UB+HF-LYP/6-31G(d,p)) (Hartree): -772.063518994

Electronic state : 1-A

Cartesian coordinates (Angs):

C	2.103986	0.682892	0.090435
O	1.310971	-0.235566	-0.597968
O	-0.523332	0.517130	-0.505534
H	-0.722838	-0.404497	-0.276244
C	-2.851756	1.458847	-0.313825
H	-1.651246	0.995559	-0.472162
H	1.755660	0.800646	1.130382
C	-2.674143	2.487130	0.787413
H	-2.297247	2.037580	1.710767
H	-1.959000	3.254952	0.481037
H	-3.625507	2.983247	1.019666
C	-3.760130	0.309578	-0.110444
C	-4.277266	-0.374043	-1.230172
C	-4.106747	-0.163843	1.170170
C	-5.109491	-1.478819	-1.078105
H	-4.017964	-0.025713	-2.226915
C	-4.942133	-1.268790	1.322047
H	-3.725212	0.339361	2.052858
C	-5.446680	-1.931888	0.200774
H	-5.498900	-1.986382	-1.955981
H	-5.201199	-1.613568	2.319119
H	-6.097158	-2.793095	0.321818
C	2.139275	2.059671	-0.583778
H	1.131239	2.480859	-0.602979
H	2.800573	2.741754	-0.038476
H	2.497680	1.975125	-1.613800
C	3.479569	0.011525	0.131577
C	4.122407	-0.226147	1.351524
C	4.109738	-0.381868	-1.057899
C	5.386828	-0.817315	1.384177
H	3.633240	0.060355	2.278999
C	5.368562	-0.980227	-1.025475
H	3.602352	-0.226221	-2.004554
C	6.012940	-1.195891	0.195457
H	5.879643	-0.985732	2.337807
H	5.847179	-1.281143	-1.953355
H	6.994892	-1.660063	0.219914
H	-2.977050	1.909584	-1.303130

Rotational constants (GHz): 0.8820000 0.1234800 0.1191500

Vibrational harmonic frequencies (cm-1):

-1370.3133	10.1123	20.2349
22.2549	34.4391	48.7320

57.5050	84.4636	120.0704
151.1142	162.3685	180.1675
187.7298	215.5944	233.9213
238.6426	270.2840	302.4142
319.9330	395.8947	413.1796
417.2365	427.5607	494.3936
509.2097	538.9690	558.1884
605.2984	631.3618	632.8180
657.6346	704.3324	711.8593
748.0005	774.0085	777.0462
788.4452	809.5190	855.1386
859.6290	870.8769	909.0109
928.1278	929.1755	972.4770
974.9977	996.7132	1000.4070
1009.8637	1015.6469	1016.0563
1027.8633	1056.6887	1056.9677
1069.7546	1088.5923	1094.3758
1107.9079	1134.8750	1145.5018
1174.6338	1185.9634	1187.5454
1202.0796	1207.7526	1209.0666
1238.8475	1291.1903	1332.4565
1359.5856	1360.0402	1364.5497
1385.8046	1388.7259	1407.0025
1422.7106	1483.6990	1491.1793
1493.8835	1497.2533	1503.0434
1509.3416	1511.8625	1533.4348
1538.2330	1626.3941	1638.4667
1650.1696	1653.7919	2970.8841
3036.5192	3051.1140	3093.3657
3107.5331	3125.7358	3134.5286
3143.6786	3175.6910	3178.6308
3183.4147	3186.0183	3192.5632
3195.9004	3203.4142	3206.0090
3212.4426	3212.8262	3810.0813

Zero-point correction (Hartree): 0.313578

RO•---H_2O

E(UB+HF-LYP/6-31G(d,p)) (Hartree): -461.860166665
Electronic state : 2-A
Cartesian coordinates (Angs):

C	-1.083781	-0.085127	0.012089
O	-1.697726	1.087500	-0.332377
O	-4.209508	-0.272347	-0.564103
H	-3.535028	0.427207	-0.591631

H	-4.368750	-0.491897	-1.489626
H	-1.496392	-0.916535	-0.587515
C	-1.589076	-0.373186	1.478154
H	-2.672182	-0.499190	1.466042
H	-1.106391	-1.292568	1.817753
H	-1.300899	0.449553	2.135418
C	0.433889	-0.050420	-0.060768
C	1.150024	-1.241807	-0.221824
C	1.130458	1.157062	0.049314
C	2.544826	-1.229237	-0.265328
H	0.614774	-2.184345	-0.318709
C	2.525042	1.170860	0.004979
H	0.570195	2.080652	0.154833
C	3.235843	-0.021377	-0.150360
H	3.090168	-2.159952	-0.393806
H	3.057653	2.114153	0.088087
H	4.321375	-0.008909	-0.186537

Rotational constants (GHz): 3.1398400 0.6176800 0.5724600

Vibrational harmonic frequencies (cm-1):

30.6719	41.0391	82.8830
131.5316	140.2987	156.2465
234.1346	258.2433	304.5446
338.3235	363.2633	414.8827
446.2386	538.6546	603.2023
631.7785	633.0818	716.0018
760.6660	780.6178	863.9572
867.2090	930.3056	934.9093
978.2240	1002.4141	1015.6665
1047.8503	1054.7086	1091.8163
1110.1412	1186.4072	1198.6949
1208.2256	1241.2284	1314.5213
1361.1019	1372.1968	1387.5113
1487.0821	1494.8998	1508.9488
1537.5610	1643.1506	1659.2858
1678.6610	2955.4984	3069.1747
3159.5116	3167.3345	3181.7407
3183.3326	3193.6224	3205.5454
3213.1400	3708.4316	3882.1518

Zero-point correction (Hartree): 0.172463