Theoretical Investigation of the Role of Intramolecular Hydrogen Bonding in β-Hydroxyethoxy and β-Hydroxyethylperoxy Radicals in the Tropospheric Oxidation of Ethene

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Theoretical investigation of the role of intramolecular hydrogen bonding in β-hydroxy-ethoxy and β-hydroxy-ethylperoxy radicals in the tropospheric oxidation of ethene.

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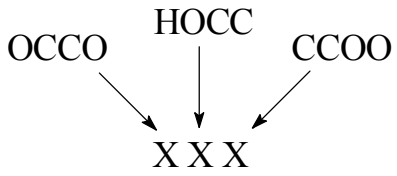
SUPPORTING INFORMATION

A. Hydroxy-eth(ylper)oxy radical geometries

The rotamers for the β-hydroxy-eth(ylper)oxy radicals and the transition states for dissociation can be paired (by inverting the sign of all dihedral angles) in enantiomers with the same energy, except the structures with C_s symmetry which are their own mirror image. As such, the tabulated material below only distinguishes between these enantiomers when listing the dihedral angles; all other characteristics are only listed once. The names of the structures are derived from the dihedral angles OCCO, HOCC, and –where applicable– CCOO, in that order :



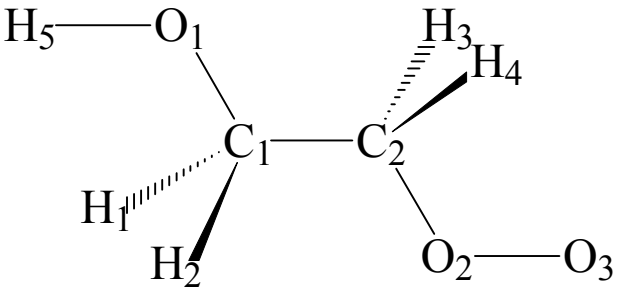
where X can have the following code :

'p' : for angles close to +60° (**p**lus)

'm' : for angles close to - 60° (**m**inus)

't' : for angles close to 180° (**t**rans)

The geometric parameters are given in Ångstroms for the bond lengths, and degrees for bond angles and dihedral angles. In all cases, the following numbering of atoms is used:



The threedimensional representations were created using Rasmol 2.5.1. The structures are sorted by increasing relative energy.

1. β-hydroxy-ethylperoxy radicals ($HOCH_2CH_2OO$)

Structure	C_1-C_2	C_1-O_1	C_2-O_2	C_1-H_1	C_1-H_2	C_2-H_3	C_2-H_4	O_1-H_5	O_2-O_3
pmm / mpp	1.5245	1.4086	1.4609	1.1027	1.0962	1.0939	1.0935	0.9697	1.3249
pmp / mpm	1.5214	1.4139	1.4614	1.0950	1.0998	1.0934	1.0929	0.9666	1.3255
pmt / mpt	1.5187	1.4142	1.4599	1.0948	1.1013	1.0951	1.0927	0.9666	1.3223
ptp / mtm	1.5144	1.4163	1.4583	1.0991	1.1029	1.0929	1.0932	0.9645	1.3225
tpp / tmm	1.5308	1.4165	1.4517	1.0983	1.0939	1.0943	1.0927	0.9658	1.3260
ttp / ttm	1.5231	1.4179	1.4514	1.1009	1.0992	1.0927	1.0922	0.9646	1.3257
tmp / tpm	1.5304	1.4169	1.4521	1.0930	1.0995	1.0922	1.0949	0.9656	1.3260
mmm / ppp	1.5231	1.4131	1.4559	1.0937	1.1024	1.0952	1.0943	0.9659	1.3230
ptt / mtt	1.5127	1.4159	1.4563	1.1007	1.1025	1.0931	1.0942	0.9647	1.3216
mmt / ppt	1.5198	1.4134	1.4550	1.0946	1.1023	1.0954	1.0956	0.9661	1.3221
ttt (C_s symm.)	1.5212	1.4177	1.4521	1.1005	1.1005	1.0932	1.0932	0.9646	1.3228
tpt / tmt	1.5272	1.4177	1.4537	1.0938	1.0995	1.0935	1.0953	0.9658	1.3234
ptm / mtp	1.5172	1.4134	1.4537	1.1036	1.1006	1.0946	1.0917	0.9645	1.3244

Structure	O_1-C_1-C_2	O_2-C_2-C_1	H_1-C_1-C_2	H_2-C_1-C_2	H_3-C_2-C_1	H_4-C_2-C_1	H_5-O_1-C_1	O_3-O_2-C_2
pmm / mpp	113.1026	111.7319	108.5059	107.9535	111.0008	112.2209	106.2278	111.9006
pmp / mpm	112.5181	110.1457	108.6851	108.3777	112.1658	111.4202	107.5531	110.8906
pmt / mpt	112.3259	106.3343	108.5831	109.3443	112.4873	111.9155	107.4306	111.6690
ptp / mtm	108.2656	111.7109	107.9699	107.9285	111.0958	111.1509	108.4458	110.7126
tpp / tmm	110.7200	110.5586	108.8413	109.6350	111.5850	111.3073	108.2483	110.7285
ttp / ttm	106.0282	110.1975	109.2636	108.4531	111.2626	111.2081	108.3099	110.8662
tmp / tpm	110.7954	110.5838	108.5453	109.8154	111.0202	111.8517	108.4213	110.7403
mmm / ppp	113.8102	111.8902	108.1504	107.9461	112.1363	110.9890	108.5723	110.6523
ptt / mtt	108.2341	108.1082	108.8666	107.7974	111.3037	111.5007	108.5713	110.7796
mmt / ppt	113.7863	108.3996	109.2660	107.7347	112.4815	111.3028	108.5044	110.8183
ttt (C_s symm.)	105.8235	106.9003	109.3251	109.3251	111.4969	111.4969	108.2435	111.0530
tpt / tmt	110.5008	107.5639	109.6679	109.9619	111.2918	112.0684	108.3270	111.1721
ptm / mtp	108.4660	110.5577	107.7484	108.6484	110.4555	111.5120	108.6023	111.8672

Structure	O_1-C_1-C_2-O_2	H_1-C_1-C_2-O_1	H_2-C_1-C_2-O_1	H_3-C_2-C_1-O_2	H_4-C_2-C_1-O_2	H_5-O_1-C_1-C_2	O_3-O_2-C_2-C_1
pmm	77.033	-125.614	118.352	-120.462	115.416	-51.069	-58.464
mpp	-77.033	125.614	-118.352	120.462	-115.416	51.069	58.464
pmp	64.559	118.091	-124.835	120.121	-114.877	-64.147	71.950
mpm	-64.559	-118.091	124.835	-120.121	114.877	64.147	-71.950
pmt	66.104	118.012	-125.027	118.040	-117.307	-61.669	-170.545
mpt	-66.104	-118.012	125.027	-118.040	117.307	61.669	170.545
ptp	-70.460	122.155	-121.426	116.017	-120.283	166.567	-69.168
mtm	70.460	-122.155	121.426	-116.017	120.283	-166.567	69.168
tpp	178.360	124.584	-117.552	120.171	-116.399	74.770	73.394
tmm	-178.360	-124.584	117.552	-120.171	116.399	-74.770	-73.394
ttp	178.152	-121.241	121.141	-116.023	120.618	178.610	73.060
ttm	-178.152	121.241	-121.141	116.023	-120.618	-178.610	-73.060
tmp	-179.249	117.328	-124.984	120.748	-115.837	-75.774	73.018
tpm	179.249	-117.328	124.984	-120.748	115.837	75.774	-73.018
mmm	-63.753	118.188	-125.585	116.418	-120.427	-67.733	-69.796
ppp	63.753	-118.188	125.585	-116.418	120.427	67.733	69.796
ptt	73.358	-122.230	121.384	-118.586	118.256	-169.569	-178.806
mtt	-73.358	122.230	-121.384	118.586	-118.256	169.569	178.806
mmt	-65.874	118.389	-125.405	118.952	-118.470	-64.505	173.968
ppt	65.874	-118.389	125.405	-118.952	118.470	64.505	-173.968
ttt (C_s symm.)	180.000	121.164	-121.164	118.641	-118.641	180.000	180.000
tpt	177.859	-117.263	124.779	-118.897	118.465	73.151	176.568
tmt	-177.859	117.263	-124.779	118.897	-118.465	-73.151	-176.568
ptm	72.566	121.495	-122.297	116.349	-119.785	-164.142	-98.696
mtp	-72.566	-121.495	122.297	-116.349	119.785	164.142	98.696

2. β-hydroxy-ethoxy radicals ($HOCH_2CH_2O$)

Structure	C_1-C_2	C_1-O_1	C_2-O_2	C_1-H_1	C_1-H_2	C_2-H_3	C_2-H_4	O_1-H_5
pm / mp	1.5400	1.4081	1.3696	1.1028	1.0951	1.1118	1.1047	0.9697
tt (C_s symm.)	1.5282	1.4200	1.3643	1.1008	1.1008	1.1095	1.1095	0.9645
tp / tm	1.5387	1.4185	1.3649	1.1001	1.0936	1.1093	1.1115	0.9657
pt / mt	1.5247	1.4182	1.3693	1.1038	1.1006	1.1094	1.1077	0.9647
pp / mm	1.5360	1.4156	1.3670	1.1030	1.0939	1.1123	1.1090	0.9662

Structure	O_1-C_1-C_2	O_2-C_2-C_1	H_1-C_1-C_2	H_2-C_1-C_2	H_3-C_2-C_1	H_4-C_2-C_1	H_5-O_1-C_1
pm / mp	110.3286	111.8905	108.5405	110.1561	107.8798	113.4605	105.4778
tt (C_s symm.)	106.6868	114.9161	108.9390	108.9390	110.3130	110.3130	108.4890
tp / tm	111.5610	114.7762	109.3756	109.0732	111.5856	108.3420	108.2192
pt / mt	107.3320	115.3553	109.1741	108.4355	110.4954	109.9128	108.4859
pp / mm	112.6544	114.9489	108.9564	108.6528	108.1748	111.1928	108.2542

Structure	O_1-C_1-C_2-O_2	H_1-C_1-C_2-O_1	H_2-C_1-C_2-O_1	H_3-C_2-C_1-O_2	H_4-C_2-C_1-O_2	H_5-O_1-C_1-C_2
pm	50.511	-123.112	119.215	-113.704	128.845	-45.740
mp	-50.511	123.112	-119.215	113.704	-128.845	45.740
tt (C_s symm.)	180.000	121.417	-121.417	123.462	123.462	180.000
tp	176.163	124.753	-117.948	128.327	-117.598	72.883
tm	-176.163	-124.753	117.948	-128.327	117.598	-72.883
pt	72.801	121.303	-121.291	121.878	-123.556	-170.508
mt	-72.801	-121.303	121.291	-121.878	123.556	170.508
pp	68.889	124.821	-117.532	116.187	-128.881	66.611
mm	-68.889	-124.821	117.532	-116.187	128.881	-66.611

3. Transition states for dissociation of β-hydroxy-ethoxy radicals, and the products

Structure	C_1-C_2	C_1-O_1	C_2-O_2	C_1-H_1	C_1-H_2	C_2-H_3	C_2-H_4	O_1-H_5
TS_pm / TS_mp	2.1531	1.3451	1.2449	1.0904	1.0875	1.1074	1.1075	0.9769
TS_tp / TS_tm	2.2218	1.3572	1.2335	1.0879	1.0842	1.1116	1.1085	0.9667
TS_pp / TS_mm	2.2107	1.3542	1.2319	1.0915	1.0844	1.1114	1.1122	0.9666
$H_2COH^{\cdots}OCH_2$	3.6469	1.3643	1.2139	1.0888	1.0845	1.1647	1.1061	0.9754

Structure	O_1-C_1-C_2	O_2-C_2-C_1	H_1-C_1-C_2	H_2-C_1-C_2	H_3-C_2-C_1	H_4-C_2-C_1	H_5-O_1-C_1
TS_pm / TS_mp	98.7001	98.0218	92.6166	111.7127	90.1318	98.2435	106.9849
TS_tp / TS_tm	110.2194	104.8800	95.8653	97.6864	89.4849	90.0051	109.7349
TS_pp / TS_mm	110.8586	107.2933	97.4364	96.9851	88.6468	89.1891	110.0182
$H_2COH^{\cdots}OCH_2$	57.4021	69.4617	87.9817	148.0578	56.7819	156.5685	108.8036

Structure	O_1-C_1-C_2-O_2	H_1-C_1-C_2-O_1	H_2-C_1-C_2-O_1	H_3-C_2-C_1-O_2	H_4-C_2-C_1-O_2	H_5-O_1-C_1-C_2
TS_pm	47.941	-119.314	119.483	-121.786	123.597	-44.934
TS_mp	-47.941	119.314	-119.483	121.786	-123.597	44.934
TS_tp	-172.381	123.335	-117.540	122.895	-123.450	81.385
TS_tm	172.381	-123.335	117.540	-122.895	123.450	-81.385
TS_pp	69.127	123.690	-116.952	123.098	-123.154	78.823
TS_mm	-69.127	-123.690	116.952	-123.098	123.154	-78.823
$H_2COH^{\cdots}OCH_2$	67.870	-126.229	82.718	-156.426	122.046	-40.513

$H_2COH^{\cdots}OCH_2$: $H_5^{\cdots}O_2$ = 1.8899 Å

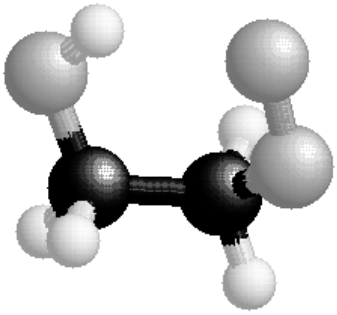
Fragments at infinite distance :

CH_2OH :
- C_1-O_1 = 1.3684
- C_1-H_1 = 1.0834
- C_1-H_2 = 1.0879
- O_1-H_5 = 0.9652
- H_1-C_1-O_1 = 112.9732
- H_2-C_1-O_1 = 118.8188
- H_2-C_1-O_1-H_1 = 148.448
- H_5-O_1-C_1-H_1 = -176.000

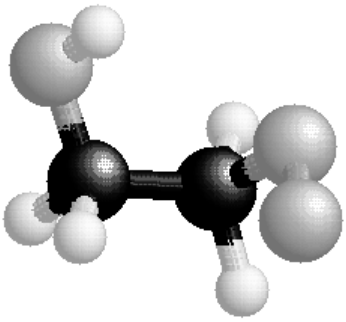
CH_2O (C_{2v} symm.) :
- C_2-O_2 = 1.2067
- C_2-H_3 = 1.1108
- H_3-C_2-O_2 = 122.3922
- H_3-C_2-O_2-H_4 = 180.000

4. Rotational constants

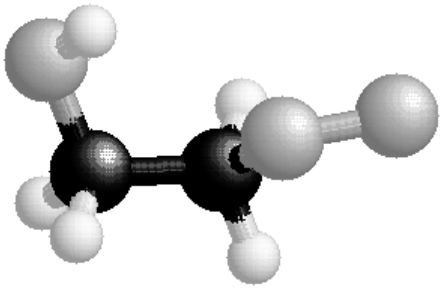
Structure	A (GHz)	B (GHz)	C (GHz)
pmm / mpp	8.7773	4.1732	3.0947
pmp / mpm	10.4832	3.2256	3.0210
pmt / mpt	13.8635	2.8164	2.5388
ptp / mtm	10.9299	3.1171	2.9822
tpp / tmm	15.9220	2.5610	2.4094
ttp / ttm	16.2941	2.5867	2.4220
tmp / tpm	16.1251	2.5620	2.3953
mmm / ppp	10.7003	3.1253	2.9568
ptt / mtt	15.2242	2.6773	2.4784
mmt / ppt	14.5676	2.6854	2.4725
ttt	25.9262	2.2262	2.1048
tpt / tmt	25.5800	2.1919	2.0836
ptm / mtp	9.5568	3.6245	2.9097
pm / mp	15.9807	5.9946	4.8257
tt	32.1855	4.1409	3.8424
tp / tm	31.6008	4.0661	3.8092
pt / mt	18.0163	5.2017	4.5842
pp / mm	17.7990	5.1096	4.5301
TS_pm / TS_mp	15.5520	5.1810	4.3219
TS_tp / TS_tm	25.3338	3.3464	3.1182
TS_pp / TS_mm	17.9025	3.8062	3.5336
$H_2COH^{\cdots}OCH_2$	19.0983	3.0560	2.9707
CH_2OH	191.2987	29.7886	26.0989
CH_2O	284.9910	38.6201	34.0112



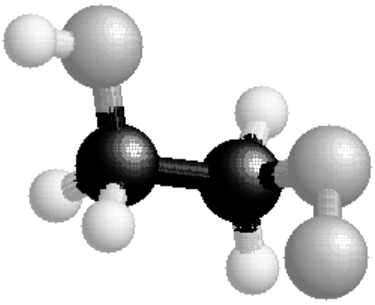
pmm / mpp



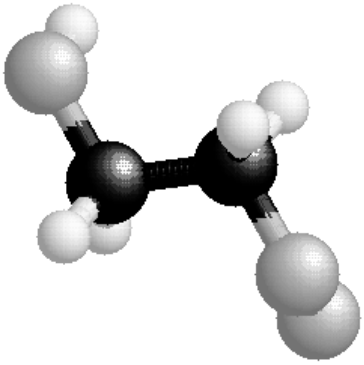
pmp / mpm



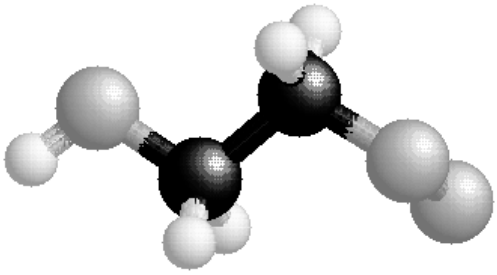
pmt / mpt



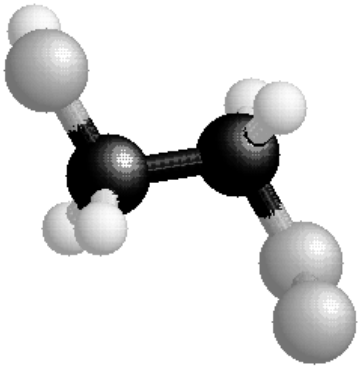
ptp / mtm



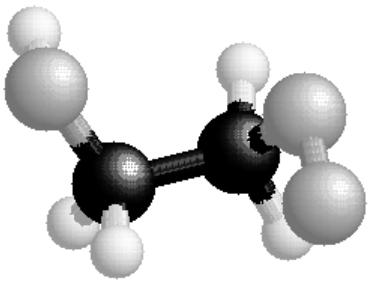
tpp / tmm



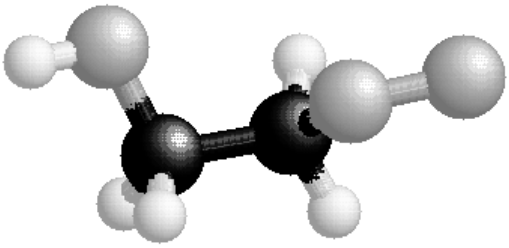
ttp / ttm



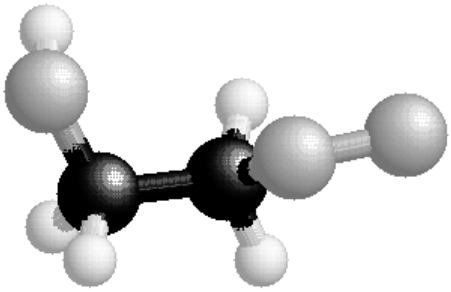
tpm / tmp



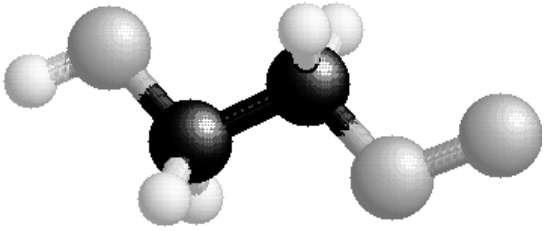
ppp / mmm



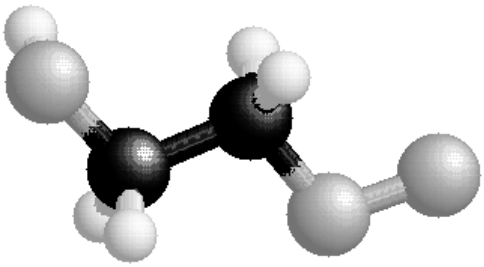
ptt / mtt



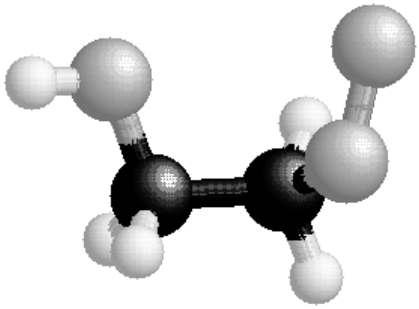
ppt / mmt



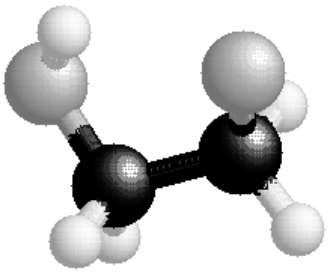
ttt (C_s symmetry)



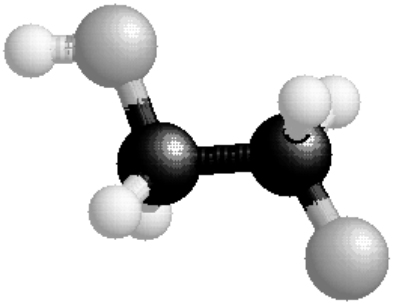
tpt / tmt



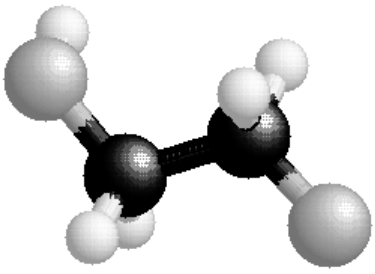
ptm / mtp



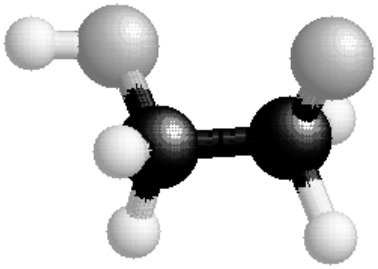
pm / mp



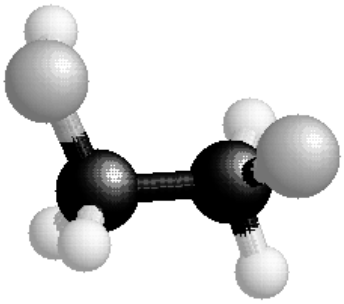
tt (C_s symmetry)



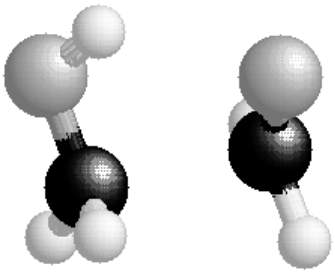
tp / tm



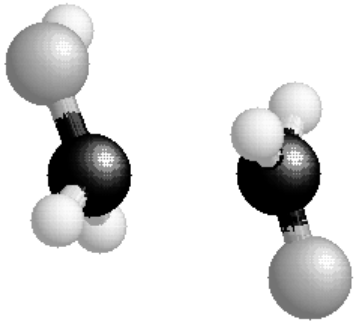
pt / mt



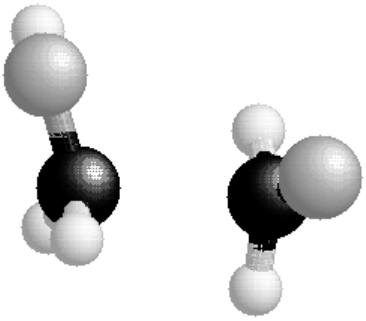
pp / mm



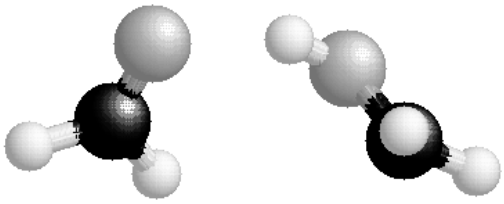
TS_pm / TS_mp



TS_tp / TS_tm

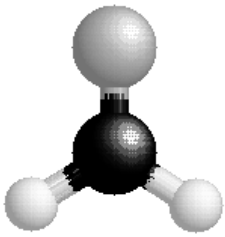


TS_pp / TS_mm



$H_2COH\cdots OCH_2$

CH_2OH



CH_2O (C_{2v} symmetry)

B. Hydroxy-eth(ylper)oxy radical vibrational frequencies

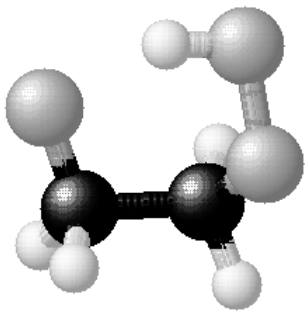
The wavenumbers listed below are given in cm^{-1}, and pertain to both enantiomers of each rotamer. All wavenumbers reported here have been scaled by 0.9614, as indicated in the main article.

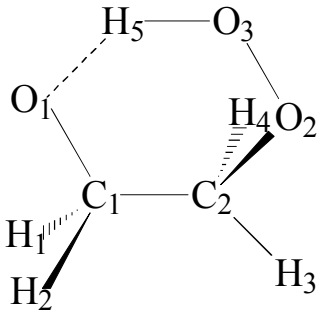
pmm	92.98	192.46	320.34	381.55	488.01	538.84	776.09	899.32	936.18	1046.21	1082.51	1130.90
	1184.09	1232.56	1322.78	1342.83	1394.67	1422.43	1452.18	2876.07	2955.22	2966.17	3022.82	3612.10
pmp	83.65	148.44	261.57	361.61	444.96	539.95	785.73	854.90	939.97	1046.46	1085.74	1118.73
	1180.82	1228.15	1322.41	1343.52	1367.60	1420.36	1450.23	2907.16	2961.83	2982.39	3030.20	3664.52
pmt	52.35	139.25	260.09	375.51	390.92	528.45	791.33	862.29	970.07	1050.05	1073.74	1153.33
	1181.61	1199.71	1326.84	1345.12	1377.33	1433.64	1449.23	2890.20	2951.56	2981.48	3019.87	3665.51
ptp	83.06	152.95	201.81	280.31	434.26	541.22	798.14	865.31	962.12	1047.74	1074.21	1128.60
	1200.46	1225.19	1264.03	1332.41	1401.12	1418.48	1466.85	2868.03	2926.30	2966.33	3030.45	3691.91
tpp	100.87	116.77	263.07	313.11	374.10	542.86	773.19	896.00	996.69	1034.93	1070.90	1116.06
	1190.35	1262.70	1282.50	1342.00	1368.33	1433.01	1468.04	2919.41	2955.95	2990.54	3027.19	3670.27
ttp	97.95	111.10	212.28	268.19	372.41	546.25	792.46	901.58	981.51	1055.24	1110.54	1138.18
	1194.50	1204.30	1257.29	1305.51	1411.06	1439.97	1486.46	2883.66	2927.75	2972.10	3036.63	3690.72
tpm	106.08	110.62	261.14	301.34	372.53	542.06	773.79	896.18	1002.41	1036.23	1062.74	1115.33
	1191.58	1258.11	1284.83	1341.39	1367.57	1434.04	1468.32	2906.67	2954.97	2999.65	3027.56	3672.25
ppp	82.32	145.16	253.55	310.72	440.97	546.58	795.20	846.50	957.67	1028.45	1070.25	1119.17
	1188.51	1244.18	1331.47	1340.60	1361.20	1422.77	1449.40	2877.09	2946.64	2992.97	3009.10	3667.94
ptt	50.73	136.97	211.73	281.70	378.47	519.78	808.53	869.14	982.86	1061.99	1079.45	1158.61
	1167.90	1225.84	1253.32	1330.96	1415.04	1430.10	1462.60	2869.55	2908.56	2957.86	3018.59	3689.60
ppt	47.42	131.10	232.35	309.63	383.31	531.41	795.73	856.93	994.24	1018.22	1078.91	1144.52
	1164.21	1233.52	1330.83	1337.80	1376.27	1436.09	1445.92	2877.87	2938.47	2979.81	2995.87	3665.66
ttt	55.30	95.54	201.93	230.60	403.91	484.46	785.96	947.36	1001.91	1058.51	1097.02	1158.17
	1166.95	1209.39	1246.66	1306.54	1423.81	1455.00	1487.81	2882.12	2916.07	2962.84	3022.59	3691.45
tpt	43.51	109.30	195.76	303.35	398.31	483.98	769.42	932.54	1018.89	1045.12	1062.50	1135.91
	1154.45	1249.47	1288.71	1343.30	1381.50	1449.55	1470.55	2905.74	2946.15	2987.05	3012.35	3670.95
ptm	52.46	126.14	188.15	301.12	451.67	493.90	802.41	879.04	954.10	1043.37	1080.18	1129.68
	1208.22	1227.36	1265.40	1328.86	1405.99	1412.45	1462.37	2859.29	2906.96	2959.72	3034.32	3692.69
pm	162.58	292.01	455.24	523.92	775.82	835.38	978.85	1035.27	1064.07	1100.24	1171.28	1218.76
	1332.25	1336.54	1379.14	1467.76	2781.62	2859.96	2875.51	2973.12	3617.66			
tt	110.58	235.83	275.24	378.19	470.63	862.28	963.81	1044.03	1060.52	1149.41	1190.36	1232.11
	1276.39	1347.54	1410.89	1480.32	2801.47	2814.41	2878.75	2916.13	3690.08			
tp	127.77	263.61	298.89	442.55	584.00	860.35	967.45	1036.14	1052.53	1081.44	1165.85	1273.72
	1310.70	1339.32	1351.39	1461.29	2783.47	2812.51	2898.88	2993.47	3671.50			
pt	136.71	201.20	301.50	324.76	526.58	845.65	942.67	1044.66	1057.94	1112.24	1213.44	1234.23
	1307.03	1344.05	1406.48	1463.88	2806.87	2836.25	2856.68	2908.05	3687.13			
pp	135.11	278.80	320.49	456.24	737.31	859.92	889.34	1002.58	1070.16	1091.39	1138.63	1266.01
	1335.40	1339.99	1364.99	1445.60	2776.35	2817.23	2866.42	2991.23	3662.92			
TS_pm	280.30i	142.29	189.70	358.45	511.34	568.39	679.11	936.65	1057.51	1087.90	1196.33	1201.28
	1344.27	1423.90	1465.29	1577.41	2801.07	2853.57	2978.56	3100.90	3503.37			
TS_tp	191.56i	61.80	151.33	339.79	375.37	552.28	659.40	916.64	1042.74	1067.17	1178.46	1198.39
	1325.38	1438.72	1453.31	1606.61	2766.84	2823.36	3008.18	3139.96	3670.27			
TS_pp	220.50i	67.07	187.22	257.12	388.85	591.72	659.67	927.60	1054.65	1056.47	1186.83	1208.72
	1328.91	1438.53	1452.40	1603.30	2754.93	2791.64	2973.28	3127.00	3670.01			
Hbonded	24.62	102.44	115.04	211.12	232.98	244.29	631.74	747.78	1069.02	1161.28	1186.87	1225.61
products	1375.85	1444.62	1478.68	1744.39	2836.80	2919.65	2992.74	3126.82	3502.78			
CH_2OH	424.51	620.48	1023.60	1175.38	1313.97	1443.08	3002.98	3142.26	3684.96			
CH_2O	1153.27	1223.98	1492.68	1776.64	2785.30	2838.99						

C. Additional calculations

1. Hydroperoxy-ethoxy radicals, OCH_2CH_2OOH

Only one rotamer was characterised; this should be the most stable structure, by analogy with the hydroxy-ethylperoxy structure pmm. All other hydroperoxy-ethoxy rotamers are expected to be higher in energy, with energy spacings comparable to those between the hydroxy-ethylperoxy structures.





B3LYP-DFT/6-31G** Energy = -304.7148054 hartree (<S**2> = 0.7542)

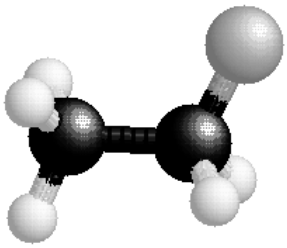
ZPE = 45.47 kcal/mol Rel. Energy = 18.77 kcal/mol above structure **pmm**

A = 8.3449 GHz B = 4.5553 GHz C = 3.2696 GHz

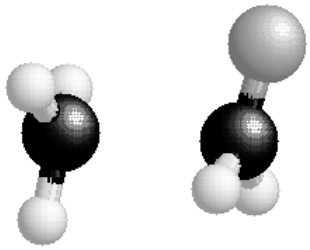
Bond lengths (Å)	Bond angles (degrees)	Dihedral Angles (degrees)
C_1-C_2 : 1.5927	O_1-C_1-C_2 : 107.311	O_1-C_1-C_2-O_2 : -61.173
C_1-O_1 : 1.3533	C_1-C_2-O_2 : 110.230	C_1-C_2-O_2-O_3 : 176.556
C_2-O_2 : 1.3953	C_2-O_2-O_3 : 107.175	C_2-O_2-O_3-H_5 : -69.824
O_2-O_3 : 1.4435	O_2-O_3-H_5 : 100.389	H_1-C_1-C_2-O_1 : 120.859
C_1-H_1 : 1.1029	H_1-C_1-C_2 : 105.329	H_2-C_1-C_2-O_1 : -121.808
C_1-H_2 : 1.1050	H_2-C_1-C_2 : 106.080	H_3-C_2-C_1-O_2 : 122.885
C_2-H_3 : 1.0934	C_1-C_2-H_3 : 109.275	H_4-C_2-C_1-O_2 : -115.995
C_2-H_4 : 1.0951	C_1-C_2-H_4 : 107.614	
O_3-H_5 : 0.9877		
O_1-H_5 : 1.8681		

Vibrational Wavenumbers (cm^{-1}) (scaled by 0.9614) : 169.72, 200.21, 335.68, 403.57, 428.69, 532.93, 741.95, 806.25, 869.91, 925.25, 1039.96, 1079.14, 1190.06, 1224.54, 1240.61, 1306.41, 1407.83, 1416.73, 1479.53, 2832.79, 2889.75, 2948.68, 3020.14, 3316.57

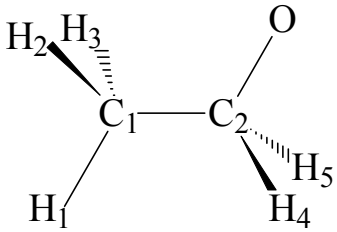
2. Ethoxy radical dissociation by C-C bond rupture



C_2H_5O radical



TS : CH_3--CH_2O (C_s)



C_2H_5O radical

B3LYP-DFT/6-31G** Energy = -154.3744648 hartree (<S**2> = 0.7530)
ZPE = 39.27 cal/mol Rel. Energy = 0.00 kcal/mol
A = 39.4932 GHz B = 9.5248 GHz C = 8.4730 GHz

Bond lengths (Å)	Bond angles (degrees)	Dihedral Angles (degrees)
C_1-C_2 : 1.5289	C_1-C_2-O : 115.442	H_1-C_1-C_2-O : 177.614
C_1-H_1 : 1.0954	H_1-C_1-C_2 : 110.979	H_2-C_1-C_2-O : 57.079
C_1-H_2 : 1.0938	H_2-C_1-C_2 : 110.469	H_3-C_1-C_2-O : -62.442
C_1-H_3 : 1.0942	H_3-C_1-C_2 : 110.340	H_4-C_2-C_1-O : 58.425
C_2-H_4 : 1.1119	H_4-C_2-C_1 : 110.709	H_5-C_2-C_1-O : -56.154
C_2-H_5 : 1.1082	H_5-C_2-C_1 : 111.928	
C_2-O : 1.3696		

Vibrational Wavenumbers (cm^{-1}) (scaled by 0.9614) : 207.79, 377.16, 431.11, 840.98, 863.64, 1044.68, 1055.01, 1193.68, 1305.54, 1339.31, 1363.32, 1442.10, 1452.27, 2781.54, 2818.66, 2932.67, 3003.42, 3014.20

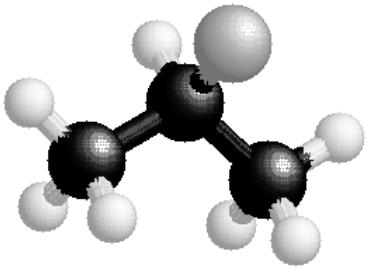
Transition state for C-C bond rupture CH_3--CH_2O (C_s symmetry)

B3LYP-DFT/6-31G** Energy = -154.3405077 hartree (<S**2> =0.7675)
ZPE = 36.89 kcal/mol Rel. Energy = 18.94 kcal/mol
A = 32.8760 GHz B = 7.2318 GHz C = 6.4546 GHz

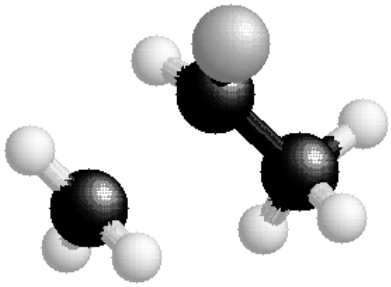
Bond lengths (Å)	Bond angles (degrees)	Dihedral Angles (degrees)
C_1-C_2 : 2.2467	C_1-C_2-O : 103.851	H_1-C_1-C_2-O : 180.000
C_1-H_1 : 1.0851	H_1-C_1-C_2 : 99.590	H_2-C_1-C_2-O : 59.670
C_1-H_2 : 1.0832	H_2-C_1-C_2 : 98.273	H_3-C_1-C_2-O : -59.670
C_1-H_3 : 1.0832	H_3-C_1-C_2 : 98.273	H_4-C_2-C_1-O : 57.281
C_2-H_4 : 1.1086	H_4-C_2-C_1 : 89.324	H_5-C_2-C_1-O : -57.281
C_2-H_5 : 1.1086	H_5-C_2-C_1 : 89.324	
C_2-O : 1.2305		

Vibrational Wavenumbers (cm^{-1}) (scaled by 0.9614) : a' : *298.28i*, 249.29, 510.69, 846.81, 1063.40, 1384.27, 1448.96, 1610.69, 2791.74, 2999.28, 3160.15; a" : 114.61, 471.13, 566.28, 1206.97, 1370.04, 2838.60, 3173.31

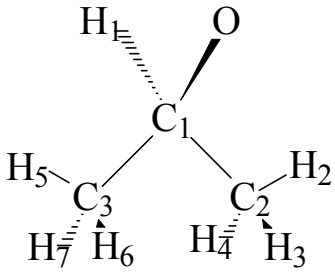
2. isopropoxy radical dissociation by C-C bond rupture



i-C_3H_7O radical



TS : CH_3--$CH(O)CH_3$



i-C_3H_7O radical

B3LYP-DFT/6-31G** Energy = -193.6946796 hartree (<S**2> = 0.7529)

ZPE = 57.08 kcal/mol Rel. Energy = 0.00 kcal/mol

A = 9.5430 GHz B = 7.9327 GHz C = 4.9810 GHz

Bond lengths (Å)	Bond angles (degrees)	Dihedral Angles (degrees)
C_1-C_2 : 1.5336	C_1-C_2-C_3 : 111.790	C_3-C_1-C_2-O : -117.519
C_1-C_3 : 1.5570	O-C_1-C_2 : 112.721	H_1-C_1-C_2-O : 124.063
C_1-H_1 : 1.1066	H_1-C_1-C_2 : 110.365	H_2-C_2-C_1-O : -59.743
C_2-H_2 : 1.0939	C_1-C_2-H_2 : 110.275	H_3-C_2-C_1-O : 59.777
C_2-H_3 : 1.0944	C_1-C_2-H_3 : 110.344	H_4-C_2-C_1-O : 180.499
C_2-H_4 : 1.0955	C_1-C_2-H_4 : 110.887	H_5-C_3-C_1-O : -62.453
C_3-H_5 : 1.0929	C_1-C_3-H_5 : 110.018	H_6-C_3-C_1-O : 58.182
C_3-H_6 : 1.0918	C_1-C_3-H_6 : 110.599	H_7-C_3-C_1-O : 178.106
C_3-H_7 : 1.0938	C_1-C_3-H_7 : 108.552	
C_2-O : 1.3744		

Vibrational Wavenumbers (cm^{-1}) (scaled by 0.9614) : 207.79, 377.16, 431.11, 840.98, 863.64, 1044.68, 1055.01, 1193.68, 1305.54, 1339.31, 1363.32, 1442.10, 1452.27, 2781.54, 2818.66, 2932.67, 3003.42, 3014.20

Transition state for C-C bond rupture CH_3--$CH(O)CH_3$

B3LYP-DFT/6-31G** Energy = -193.6660284 hartree (<S**2> = 0.7688)

ZPE = 54.27 kcal/mol Rel. Energy = 15.17 kcal/mol

A = 8.8061 GHz B = 6.4215 GHz C = 4.2141 GHz

Bond lengths (Å)	Bond angles (degrees)	Dihedral Angles (degrees)
C_1-C_2 : 1.5214	C_1-C_2-C_3 : 100.744	C_3-C_1-C_2-O : -108.852
C_1-C_3 : 2.1787	O-C_1-C_2 : 121.928	H_1-C_1-C_2-O : 158.744
C_1-H_1 : 1.1117	H_1-C_1-C_2 : 114.664	H_2-C_2-C_1-O : -80.743
C_2-H_2 : 1.0978	C_1-C_2-H_2 : 107.945	H_3-C_2-C_1-O : 36.942
C_2-H_3 : 1.0927	C_1-C_2-H_3 : 110.394	H_4-C_2-C_1-O : 160.510
C_2-H_4 : 1.0934	C_1-C_2-H_4 : 112.492	H_5-C_3-C_1-O : -65.373
C_3-H_5 : 1.0840	C_1-C_3-H_5 : 99.260	H_6-C_3-C_1-O : 53.747
C_3-H_6 : 1.0834	C_1-C_3-H_6 : 99.275	H_7-C_3-C_1-O : 174.221
C_3-H_7 : 1.0854	C_1-C_3-H_7 : 101.296	
C_2-O : 1.2401		

Vibrational Wavenumbers (cm^{-1}) (scaled by 0.9614) : *298.28i* ,114.61, 249.29, 471.13, 510.69, 566.28, 846.81, 1063.40, 1206.97, 1370.04, 1384.27, 1448.96, 1610.69, 2791.74, 2838.60, 2999.28, 3160.15, 3173.31