Electronic Supplementary Material for PCCP

On the thermal unimolecular decomposition of the cyclohexoxy radical – an experimental and theoretical study

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Electronic supplementary information

Table 1 Experimental conditions and rate coefficients k_1, k_{-1} and k_4 determined from fitting the biexponential rate law, eqn (15), to the experimental profiles.

T / K	P / bar	k_1 / s^{-1}	k_{-1} / s^{-1}	k_4 / s^{-1}
293	10.4	53756	9512	14606
	10.3	54912	16083	29050
	10.2	45933	7205	13860
	10.0	51109	22663	15167
	10.0	45391	14807	16637
	4.9	39399	14629	12102
	22.9	61143	10234	20585
	22.9	57226	11662	18385
	22.0	59521	11472	22698
	21.2	53356	12595	18411
297	20.0	70718	12757	16101
	19.6	77292	15000	18286
298	8.3	60658	19220	14193
	8.1	72142	25138	23984
301	18.7	89311	17950	19269
	18.2	91075	18488	18616
	17.8	95098	18508	23579
302	14.7	87032	21717	12319
	14.4	93940	21940	14997
	18.5	92965	17708	16800
	18.1	95159	23310	19198
310	9.1	126926	38812	19168
	4.4	83771	22952	17734
	4.2	124456	47551	23638
312	17.0	116304	34699	13351
	16.5	154213	30473	19751
	16.0	160164	32033	19662
	17.0	145711	29632	23234
	16.5	134324	23466	16100
	16.0	147104	32665	20676
315	9.9	153316	45329	97371
316	15.2	198164	41119	21365
	14.9	181086	32189	19841
	14.4	169602	32743	17423

318	9.9	205111	39486	61159
	9.7	172194	51125	43557
	9.7	205924	31740	26439
321	15.2	229862	42961	23106
	14.7	222564	45416	18772
	14.3	238071	43667	20288
323	7.9	224186	52102	26328
	7.6	210825	58214	26064
	7.3	235585	68410	58175
	55.3	241316	30584	12132
	54.7	307862	57149	42978
326	12.2	280059	50514	31656
	12.0	300855	58309	26981
	11.8	277619	56438	20752
329	50.8	379841	78550	52752
	50.4	260069	26945	40023
	50.0	393192	41880	8518
	49.6	456768	66411	45071
	49.3	343216	24533	10267
331	13.5	366103	60637	21921
	13.1	332629	61027	30121
	12.7	379482	58522	30656
332	7.5	624655	54854	36180
	6.7	631324	79576	74824
334	11.6	490745	75147	30795
	11.2	446994	65051	26640
	10.7	492397	63443	25868
339	12.1	682987	100774	54372
	11.6	665397	73058	19105
	11.2	631292	73317	21232
	10.7	662372	98340	27468
341	9.6	891779	91741	52683
	9.1	920933	91721	33946
	8.6	893002	84179	36254

Table 2 Rotational constants (*A*, *B*, *C*) and harmonic wavenumbers (ω_i) of molecular and transition state species as obtained from G3MP2B3 level of theory. The wavenumbers are scaled by 0.961.

Species	***A*, *B*, *C* / cm^{-1}**	**ω_i / cm^{-1}**
CHE	0.142 0.077 0.055	148.7, 217.4, 296.5, 317.4, 385.8, 404.7, 438.4, 531.4, 750.3, 760.1, 816.0, 816.9, 845.6, 870.5, 948.9, 955.6, 994.1, 1021.5, 1025.7, 1055.9, 1108.9, 1127.9, 1169.7, 1182.5, 1240.0, 1251.8, 1254.4, 1296.8, 1327.9, 1331.0, 1343.0, 1345.9, 1450.2, 1454.8, 1455.7, 1462.0, 1476.1, 2730.2, 2901.8, 2902.9, 2910.8, 2918.7, 2923.5, 2954.9, 2955.5, 2959.5, 2974.3, 2976.7

CHA	0.120 0.090 0.066	136.3, 192.3, 285.1, 352.7, 380.3, 417.1, 462.1, 634.5, 745.6, 751.6, 810.2, 833.9, 836.3, 874.8, 921.3, 942.0, 995.6, 996.9, 1015.1, 1040.0, 1076.7, 1110.9, 1154.8, 1176.5, 1250.0, 1253.8, 1263.8, 1308.2, 1331.6, 1333.3, 1343.8, 1346.9, 1441.8, 1449.8, 1457.1, 1460.9, 1474.1, 2751.3, 2900.9, 2912.7, 2916.8, 2917.5, 2924.2, 2953.7, 2958.4, 2962.6, 2977.1, 2978.9
TBI	0.135 0.081 0.061	71.6, 191.1, 248.6, 347.6, 383.6, 407.2, 504.7, 540.4, 733.0, 752.1, 800.3, 810.8, 846.1, 917.0, 929.0, 968.9, 992.5, 1011.8, 1064.5, 1080.4, 1118.6, 1140.4, 1189.8, 1216.2, 1241.2, 1257.7, 1287.9, 1293.3, 1314.4, 1332.3, 1343.5, 1359.1, 1450.0, 1457.2, 1458.3, 1470.2, 1482.1, 2828.9, 2915.7, 2922.4, 2927.5, 2933.7, 2946.3, 2954.0, 2965.9, 2974.4, 2978.1, 3004.9
TBE	0.139 0.077 0.056	91.3, 160.0, 245.9, 298.3, 381.2, 413.0, 445.2, 546.6, 732.3, 750.3, 816.1, 827.1, 851.3, 876.0, 925.9, 953.2, 1004.2, 1033.4, 1048.4, 1063.3, 1106.6, 1137.6, 1164.6, 1174.8, 1234.5, 1246.1, 1252.7, 1293.0, 1311.5, 1327.1, 1336.3, 1343.6, 1455.0, 1456.1, 1464.9, 1471.1, 1484.0, 2736.8, 2907.9, 2920.8, 2926.7, 2931.1, 2936.8, 2954.1, 2960.6, 2969.1, 2981.1, 2988.5
TBA	0.112 0.094 0.071	77.5, 152.2, 250.5, 320.9, 348.5, 451.2, 473.2, 637.8, 741.7, 748.9, 811.5, 830.2, 831.8, 855.2, 906.9, 939.4, 995.1, 1002.1, 1019.6,1061.2, 1092.4, 1115.0, 1145.9, 1180.1, 1227.3, 1253.5, 1267.2, 1298.3, 1308.7, 1324.8, 1337.2, 1343.2, 1445.3, 1448.7, 1461.2, 1465.6, 1477.4, 2763.9, 2908.7, 2917.2, 2924.2, 2933.3, 2938.1, 2959.3, 2961.5, 2972.3, 2985.0, 2990.3
l-$C_6H_{11}O$	0.333 0.030 0.028	51.0, 93.2, 106.7, 112.3, 137.9, 174.7, 217.9, 346.8, 394.3, 451.2, 651.9, 677.2, 708.8, 782.4, 852.5, 875.1, 928.6, 1000.5, 1021.0, 1048.1, 1050.2, 1110.1, 1140.1, 1218.1, 1232.7, 1278.2, 1290.7, 1295.8, 1349.3, 1369.8, 1380.9, 1423.0, 1429.7, 1440.9, 1456.6, 1473.8, 1761.8, 2779.2, 2817.8, 2892.6, 2902.4, 2914.2, 2914.9, 2933.2, 2937.7, 2972.0, 3038.2, 3132.4
TS CHE → l-$C_6H_{11}O$	0.129 0.074 0.052	310.5i, 120.0, 188.5, 273.6, 298.8, 326.5, 373.9, 438.1, 516.8, 602.9, 746.8, 775.3, 794.9, 832.9, 859.8, 867.5, 930.0, 968.1, 981.7, 1034.6, 1064.3, 1106.0, 1151.1, 1172.8, 1231.6, 1241.6, 1307.2, 1331.8, 1347.1, 1349.0, 1353.2, 1430.1, 1432.5, 1439.7, 1457.0,1464.8, 1554.8, 2758.5, 2852.0, 2900.8, 2907.6, 2913.8, 2934.5, 2954.8, 2960.2, 2966.9, 3027.6, 3116.8
TS CHA → l-$C_6H_{11}O$	0.112 0.086 0.062	332.6i, 131.7, 188.6, 240.4, 322.7, 342.8, 369.5, 459.2, 593.4, 604.5, 754.2, 774.4, 806.1, 829.9, 848.9, 872.1, 918.6, 958.3, 989.2, 1018.4, 1066.3, 1091.5, 1147.1, 1173.9, 1237.8, 1246.9, 1321.2, 1331.1, 1341.6, 1348.7, 1353.2, 1425.7, 1436.4, 1443.9, 1456.2, 1465.8, 1546.9, 2788.4, 2857.2, 2903.8, 2905.7, 2934.1, 2948.7, 2952.8, 2964.4, 2977.2, 3010.8, 3108.4
TS CHE β-C-H	0.139 0.078	813.7i, 136.1, 201.5, 321.3, 384.4, 385.3, 434.3, 459.5, 483.2, 531.1, 587.0, 719.6, 727.7, 813.6, 841.8, 878.1,

	0.055	885.6, 965.8, 995.7, 1042.4, 1047.1, 1094.4, 1100.7, 1195.5, 1215.0, 1239.0, 1248.1, 1299.9, 1313.7, 1331.0, 1343.2, 1344.6, 1428.7, 1435.3, 1457.1, 1460.0, 1472.8, 1602.2, 2893.3, 2898.9, 2905.4, 2914.0, 2918.0, 2958.7, 2959.1, 2963.3, 2992.2, 2993.1
TS CHA β-C-H	0.127 0.085 0.061	856.2i, 124.8, 184.0, 293.2, 373.0, 381.6, 425.5, 462.5, 492.2, 495.5, 686.6, 718.5, 752.4, 805.7, 847.3, 859.0, 903.2, 962.7, 990.0, 1025.0, 1037.7, 1086.8, 1099.8, 1185.2, 1200.4, 1226.9, 1252.0, 1294.5, 1302.5, 1322.1, 1336.3, 1342.9, 1439.2, 1446.2, 1456.1, 1459.1, 1471.8, 1607.6, 2908.3, 2922.5, 2923.5, 2931.8, 2937.8, 2958.0, 2965.1, 2969.7, 3004.1, 3005.6
TS CHE → TBI	0.134 0.078 0.056	196.6i, 42.5, 271.7, 331.5, 387.0, 405.1, 438.6, 593.2, 692.3, 729.1, 800.2, 821.1, 854.3, 914.3, 925.0, 969.0, 1007.1, 1031.5, 1068.4, 1094.5, 1110.8, 1171.2, 1186.6, 1232.5, 1247.0, 1263.6, 1294.6, 1297.1, 1318.2, 1342.9, 1345.3, 1351.2, 1451.3, 1458.7, 1460.4, 1471.0, 1489.4, 2805.4, 2913.0, 2918.2, 2928.4, 2940.2, 2942.7, 2953.6, 2958.8, 2970.4, 2988.7, 3000.8
TS CHE → TBE	0.138 0.077 0.054	215.5i, 37.5, 187.7, 241.6, 390.3, 422.6, 452.2, 633.6, 709.6, 748.0, 773.2, 813.6, 847.1, 895.2, 919.0, 966.0, 1018.2, 1056.0, 1067.8, 1081.9, 1131.2, 1186.2, 1224.5, 1234.6, 1245.9, 1265.9, 1281.9, 1301.5, 1315.1, 1326.2, 1343.8, 1347.0, 1457.1, 1459.6, 1470.3, 1479.1, 1493.5, 2811.8, 2925.1, 2929.3, 2934.3, 2946.4, 2951.3, 2956.3, 2965.1, 2976.6, 2985.0, 3002.5
TS CHE → TBA	0.128 0.080 0.058	163.5i, 14.1, 290.5, 299.1, 375.2, 422.8, 445.2, 595.3, 692.6, 741.1, 812.4, 823.9, 854.4, 889.6, 926.0, 941.0, 1010.4, 1035.7, 1045.5, 1067.2, 1115.1, 1152.1, 1161.7, 1194.1, 1248.7, 1250.4, 1262.2, 1304.9, 1320.4, 1328.6, 1345.3, 1349.6, 1452.6, 1457.5, 1462.5, 1470.0, 1483.2, 2746.1, 2906.5, 2912.9, 2920.5, 2934.8, 2941.9, 2953.3, 2956.7, 2963.3, 2978.7, 2991.7
TS CHA → TBI	0.126 0.085 0.061	204.4i, 48.1, 252.5, 316.7, 366.1, 420.4, 518.2, 615.0, 709.3, 720.6, 801.1, 811.2, 843.3, 905.3, 929.2, 950.3, 1003.4, 1031.8, 1063.9, 1102.3, 1127.3, 1162.6, 1219.0, 1244.3, 1247.3, 1266.4, 1292.0, 1310.3, 1314.7, 1340.4, 1347.3, 1372.3, 1450.5, 1454.8, 1462.8, 1466.2, 1485.9, 2845.6, 2912.1, 2915.9, 2930.1, 2935.7, 2950.4, 2953.4, 2965.7, 2967.9, 2974.0, 2994.8
TS CHA → TBE	0.135 0.078 0.055	152.6i, 46.4, 285.9, 351.0, 378.9, 406.6, 456.8, 583.6, 692.8, 741.0, 820.2, 846.7, 853.4, 892.0, 931.1, 953.5, 1013.1, 1048.9, 1057.1, 1070.8, 1101.8, 1147.8, 1151.9, 1170.9, 1244.7, 1251.6, 1260.0, 1302.9, 1323.6, 1335.8, 1343.1, 1347.1, 1452.6, 1457.0, 1464.0, 1468.7, 1483.3, 2740.7, 2902.7, 2911.6, 2920.6, 2922.5, 2944.9, 2955.2, 2957.4, 2960.4, 2984.7, 2990.7
TS CHA → TBA	0.111 0.094 0.069	218.7i, 64.1, 192.5, 298.8, 345.9, 469.6, 514.6, 685.1, 713.5, 732.9, 781.8, 801.2, 827.9, 923.5, 931.3, 935.5, 1019.8, 1025.8, 1057.8, 1083.9, 1127.0, 1155.2, 1216.6, 1244.4, 1248.2, 1267.9, 1276.3, 1304.0, 1318.6, 1346.6,

		1351.6, 1374.0, 1450.2, 1454.5, 1466.6, 1473.5, 1490.7, 2834.4, 2917.6, 2926.8, 2935.2, 2941.4, 2952.0, 2955.6, 2961.6, 2974.6, 2990.4, 2998.1

Table 3 Reduced moments of inertia ($I_{red,i}$; eqn (9)), Fourier coefficients (a_i, $b_{i,k}$, $c_{i,l}$; eqn (10)), and wavenumbers ω_i* (eqn (14)) for the internal rotations of l-$C_6H_{11}O$. The internal rotations are labelled successively starting from the C-C-bond next to the oxygen atom. The Fourier coefficients are arranged in ascending order of k and l, respectively, with $l_{min} = k_{min} = 1$.

C-C-bond *i*	**$I_{red,i}$ / (10^{-47} kg m^2)**	**Fourier coefficients**			**ω_i* / cm^{-1}**
		a_i / cm^{-1}	**$b_{i,k}$ / cm^{-1}**	**$c_{i,l}$ / cm^{-1}**	
1	26.4	453.34	-113.20 -104.47 -201.60 -23.60 12.06 3.08 -1.49	-6.45 0.89	79.6
2	119.0	706.67	-613.79 422.90 -554.81 28.02 14.04 5.75 -8.78	-12.17 10.89 -5.50	39.6
3	56.6	788.11	-401.76, 178.52, -585.30, 18.08, -10.09, 15.65, -3.21	-6.43 6.11 -4.41 -0.71 1.00 -0.69	66.8
4	49.5	706.58	-300.82 185.43 -622.28 5.34 21.09 8.02 -3.37	8.93 -24.65 21.79 -28.26 6.44 -1.85	70.8
5	2.9	28.22	-2.58 -6.11 -0.96 -3.64 -1.36 -14.26 0.70	1.10 10.56 -4.21 -4.75 -0.88 2.57 -0.68	108.3