Supplementary Material for PCCP

Supporting information:

"The contribution of tunnelling to the 1,5 H-shift isomerisation reaction of alkoxyl radicals"

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I. Geometries of relevant molecular configurations

I.(A). 1-butoxyl geometries (XYZ-Files, coordinates in Angstroms):

Educt molecule:

MP2(full)/6-31G(d) optimised:

```
14
1-Butoxy  Molekül in C1  (UMP2(Full)/6-31G(d) opt&freq) MP2=-232.210109
1  C  -2.3366765133  -0.1153267354  -0.132672118
2  C  -0.9030385886  -0.3498870126   0.3284914633
3  H  -3.0110451137  -0.8823102207   0.2577977028
4  H  -2.7038236752   0.8582902634   0.2057617509
5  H  -2.4023160018  -0.1358009277  -1.2244810368
6  C   0.0629478046   0.7044750228  -0.1974192333
7  H  -0.8648631405  -0.3573064578   1.4252967091
8  H  -0.5587671124  -1.334620651   -0.0025339218
9  C   1.5031133589   0.4329014721   0.2114212983
10 H   0.0121963713   0.7410482356  -1.2921818228
11 H  -0.2270441978   1.6993101331   0.1652488389
12 H   2.1870629497   1.2381375551  -0.0987576044
13 H   1.5948058072   0.3692741963   1.3103419718
14 O   2.001964718   -0.778624826   -0.2506776311
```

MP2(fc)/6-311G(d,p) optimised:

```
14
1-Butoxy Molekül in C1 (UMP2(fc)/6-311G(d,p) opt&freq)  MP2=-232.35098137783
1  C  -2.3400996967  -0.1202982877  -0.1332233612
2  C  -0.9048945824  -0.3475389135   0.3400688101
3  H  -3.0159852559  -0.8830548593   0.2638402251
4  H  -2.7069689435   0.8589848031   0.1910302018
5  H  -2.3957543115  -0.1550315229  -1.22588243
6  C   0.0632270813   0.7077463847  -0.1904912133
7  H  -0.8720386776  -0.3419335857   1.4373855955
8  H  -0.5552942681  -1.3334718733   0.0174262977
9  C   1.510123499    0.4268215693   0.2064576402
10 H   0.0032992028   0.7462182155  -1.2851455759
11 H  -0.2196817848   1.7010528966   0.1818394942
12 H   2.1881494576   1.2438693594  -0.0845640014
13 H   1.5952039197   0.3443210914   1.305721975
14 O   2.0011166068  -0.7726673802  -0.2673153796
```

TS_iso (isom. -> δ-hydroxy-butyl)

MP2(full)/6-31G(d) optimised:

```
14
1-Butoxy Isomerisierung TS  (UMP2(Full)/6-31G(d) opt&freq)
1  C   1.2947006085  -0.8907114131  -0.0606453041
2  C  -1.2821476874   0.2674409463   0.2399372194
3  C  -0.1454699303   1.1169595994  -0.3273231261
4  C   1.1746069322   0.5882690343   0.23309963
5  H   1.562031038   -1.1229071238  -1.0922947526
6  H   1.8810555017  -1.4732544289   0.6510623901
7  H  -2.242189726    0.5827976462  -0.1916581957
8  H  -1.3389438586   0.4043079816   1.3317921555
9  H  -0.2938556561   2.1722431275  -0.0721475077
10 H  -0.1521749694   1.0287891865  -1.4191770822
11 H   1.1986013271   0.7591853915   1.3149555182
12 H   2.0208515572   1.1385156741  -0.1971697784
13 O  -1.125695457   -1.0862319149  -0.1076860818
14 H   0.1200489038  -1.2915711372   0.0257153919
```

MP2(fc)/6-311G(d,p) optimised:

```
14
1-Butoxy Iso (UMP2(fc)/6-311G(d,p) opt(vt)&freq)   MP2=-232.32811324287
1  C   1.2926386145  -0.8933821895  -0.0602775077
2  C  -1.2786580395   0.2622257208   0.2495772606
3  C  -0.146484995    1.1142256366  -0.3342077027
4  C   1.1803420296   0.5933655859   0.2271882343
5  H   1.5809399343  -1.1237560927  -1.0876733776
6  H   1.8694989178  -1.4734298297   0.6616778007
7  H  -2.2400932058   0.589579755   -0.1709744454
8  H  -1.3127910021   0.3982100732   1.3422540919
9  H  -0.301302362    2.1702575641  -0.0869985847
10 H  -0.1570522754   1.0087389904  -1.4249349828
11 H   1.2032946843   0.7703085365   1.3084435672
12 H   2.0219551028   1.1422544335  -0.2128397168
13 O  -1.1362376523  -1.0830459139  -0.1039054934
14 H   0.1384257671  -1.2764046419   0.0086078875
```

TS (decomp.1 -> $CH_2O + C_3H_7$)

MP2(full)/6-31G(d) optimised:

```
14
1-Butoxy TS  (UMP2(Full)/6-31G(d) opt&freq)
1  C  -2.4253017639  -0.1466173778  -0.0860232021
2  C  -0.9484703323  -0.3371506059   0.2791268203
3  H  -3.0211195774  -0.9836495623   0.2876263861
4  H  -2.8256064631   0.7737179235   0.3476511654
5  H  -2.5563892985  -0.0958398715  -1.1699795563
6  C  -0.1137921424   0.7953701389  -0.2253752892
7  H  -0.8483418717  -0.4148140931   1.3669234362
8  H  -0.5707185951  -1.2699901806  -0.1453788841
9  C   1.8373444644   0.3212422417   0.2596151929
10 H   0.0154555714   0.8698420066  -1.3011294058
11 H  -0.1933025303   1.7542098071   0.2850566701
12 H   2.2083184207   1.2630708113  -0.1904566688
13 H   1.6019996528   0.413769448    1.3387684514
14 O   2.0113779171  -0.7634228337  -0.2728928408
```

MP2(fc)/6-311G(d,p) optimised:

```
14
1-Butoxy TS (UMP2(fc)/6-311G(d,p) opt&freq)  MP2=-232.31598174039
1  C  -2.4264838459  -0.1491388373  -0.0876702712
2  C  -0.9460483401  -0.3363830315   0.2824239945
3  H  -3.0206382159  -0.9875060206   0.2868438883
4  H  -2.8272564729   0.7726095861   0.3439974027
5  H  -2.5516165686  -0.1005113132  -1.1730235242
6  C  -0.1097703164   0.7995104726  -0.2223288471
7  H  -0.8482661     -0.4096842549   1.3709309561
8  H  -0.5663498338  -1.2685730531  -0.1425203522
9  C   1.8358388405   0.3174049406   0.2548252293
10 H   0.0176791423   0.8724879694  -1.2991457056
11 H  -0.1823794993   1.7545516337   0.2967698151
12 H   2.206077459    1.2600112191  -0.1988793588
13 H   1.5908220185   0.4109237854   1.3341594434
14 O   2.0075887553  -0.7615838523  -0.2728291498
```

I.(B). 2-pentoxyl geometries (XYZ-Files, coordinates in Angstroms):

Educt molecule:

MP2(full)/6-31G(d) optimised:

```
17
2-Pentoxy Molekül in C1 (MP2(Full)/6-31G(d) opt&freq (qc)) MP2=-271.38601679624
1  C   2.7671430202  -0.2452241595  -0.1546304191
2  C   1.4372394035   0.3474177464   0.2972291071
3  H   3.6075049499   0.3841569811   0.1510089913
4  H   2.9202740345  -1.240514975    0.2735594803
5  H   2.8000313676  -0.3418367011  -1.2439302761
6  C   0.247290835   -0.5108203475  -0.1124024018
7  H   1.4380500388   0.464184569    1.3884557209
8  H   1.3086418297   1.3489240602  -0.1234146652
9  C  -1.0983284592   0.0992948872   0.2771347514
10 H   0.2510331117  -0.6585912854  -1.2002095498
11 H   0.3277576707  -1.5080209219   0.3390496456
12 C  -2.2916494669  -0.7979203999  -0.0355276048
13 H  -1.0891731907   0.3200799523   1.3622565384
14 O  -1.2715858499   1.3667162038  -0.2774554861
15 H  -3.2199176429  -0.3080155498   0.2649357621
16 H  -2.3353681884  -0.9961841405  -1.1097716215
17 H  -2.2063191772  -1.7543979795   0.4868832663
```

TS_iso (isom. -> δ-hydroxy-pentyl)

MP2(full)/6-31G(d) optimised:

```
2-Pentoxy Iso TS in C1 (MP2(Full)/6-31G(d) opt&freq) MP2=-271.35938796941
1  C  -1.9163542071  -0.6536492055   0.1419216814
2  C  -1.5327528813   0.7700562402  -0.1973476818
3  H  -2.1474273176  -0.8161410095   1.1955357892
4  H  -2.6572065768  -1.1174812306  -0.5106875802
5  H  -0.8549504558  -1.2726595343  -0.0173449174
6  C  -0.0987399231   1.0354096771   0.257277478
7  H  -1.6022262781   0.9299464265  -1.2789012702
8  H  -2.2227760073   1.4803042339   0.2755462592
```

```
9  O   0.4193253403  -1.308245482    0.0218503615
10 C   0.8253106847  -0.0135910412  -0.3631951379
11 H   0.2305242586   2.0416719824  -0.026963275
12 H  -0.0274400675   0.952747247    1.3485849649
13 H   0.7857360649   0.0934568801  -1.4615403728
14 C   2.2679538008   0.137312323    0.102313372
15 H   2.314327781    0.0522188085   1.1904240035
16 H   2.6615238298   1.1124764089  -0.1997090168
17 H   2.8928072032  -0.643804318   -0.3355657469
```

TS (decomp.1 -> $CH_3CHO + C_3H_7$)

MP2(full)/6-31G(d) optimised:

```
17
2-Pentoxy TS1 in C1 (MP2(Full)/6-31G(d) opt&freq) MP2=-271.35264290527
1  C   2.8638002877  -0.2161747169  -0.110355922
2  C   1.4803139714   0.3545965463   0.2204337363
3  H   3.6445589845   0.5089951807   0.1345808741
4  H   3.0624041121  -1.1301911664   0.4560756859
5  H   2.9453289837  -0.4529116848  -1.1744896724
6  C   0.3976031134  -0.6215072002  -0.1118829722
7  H   1.4346766608   0.6082714907   1.2849417604
8  H   1.3040645532   1.2773156198  -0.3358029036
9  C  -1.3692349037   0.2720880057   0.3460040178
10 H   0.2097098528  -0.8011680984  -1.167026906
11 H   0.3183783193  -1.511769584    0.510594649
12 C  -2.3489362617  -0.8106302718  -0.0648691984
13 H  -1.0869755828   0.2407750474   1.4220665702
14 O  -1.2670466977   1.3194413145  -0.2895647218
15 H  -3.3409528171  -0.4924116557   0.2726419044
16 H  -2.370269822   -0.8941031685  -1.152350001
17 H  -2.1258269053  -1.7785666755   0.3893078452
```

TS (decomp.2 -> $C_3H_7CHO + CH_3$)

MP2(full)/6-31G(d) optimised:

```
17
2-Pentoxy TS2 in C1 (MP2(Full)/6-31G(d) opt&freq) MP2=-271.34771231054
1  H   3.6781354527   0.2539544668   0.0737672221
2  C   2.7943484613  -0.3499693206  -0.1492369303
3  C   1.5151218859   0.3830596628   0.2371190735
4  H   2.8038139559  -0.5776489381  -1.218979993
5  H   2.8860458468  -1.2941169836   0.3958013215
6  C   0.2601410758  -0.4366684169  -0.0754828596
7  H   1.5366128657   0.6248113547   1.3069549015
8  H   1.4422850138   1.3339918336  -0.2989656282
9  C  -0.9562947578   0.3673362603   0.3439028537
10 H   0.19962402    -0.6241067056  -1.1519907878
11 H   0.2975504783  -1.3988738384   0.4480850591
12 C  -2.4579866971  -0.960435403   -0.0521566083
13 H  -1.1897215829   0.3032872124   1.4306960746
14 O  -1.3442383881   1.3288300243  -0.3150531449
15 H  -3.3210414687  -0.3928747525   0.2690149872
16 H  -2.3382222572  -1.0722420988  -1.1217200863
17 H  -2.173155028   -1.806758441    0.5628889143
```

II. Vibrational Frequencies (unscaled)

1-butoxyl						2-pentoxyl			
MP2(fu)/6-31G(d)			MP2(fc)/6-311G(d,p)			MP2(fu)/6-31G(d)			
mol	isom.	dec.1	mol*	isom.*	dec.1*	mol	isom.	dec.1	dec.2
[a](94.7)	-2267.5	-589.4	[a](87.0)	-2033.3	-566.1	[d](83.1)	-2256.7	-655.7	-738.5
[b](152.1)	172.4	[a](72.1)	[b](151.5)	169.3	[a](61.6)	[e](118.7)	122.0	[d](67.1)	[e](86.2)
253.1	325.4	[b](118.8)	244.0	323.1	[b](118.9)	179.1	[f](248.5)	[e](92.4)	[d](102.3)
[c](263.0)	406.9	180.8	[c](251.3)	400.3	175.6	[f](237.7)	263.6	148.9	146.0
352.6	463.5	[c](259.4)	345.5	458.0	[c](252.2)	[g](261.6)	305.0	[f](209.9)	[f](171.8)
519.3	511.5	337.3	521.7	502.9	334.5	327.1	398.0	[g](259.0)	[g](259.1)
564.2	685.2	392.9	604.5	708.0	386.2	382.0	465.6	267.0	265.3
776.5	853.0	645.1	767.5	838.0	633.0	452.7	497.8	344.7	356.6
884.1	882.9	712.4	868.8	871.0	683.4	484.7	501.4	419.8	432.2
906.4	928.3	787.2	895.4	923.7	771.3	768.0	718.2	513.8	537.5
993.0	976.1	938.7	979.0	962.0	918.4	865.7	831.5	693.7	661.3
1056.9	992.3	946.4	1047.6	978.3	928.3	893.0	889.9	789.0	682.6
1090.4	1071.9	953.0	1077.5	1059.9	935.2	936.4	929.8	892.4	776.9
1121.0	1114.1	1076.8	1107.0	1099.2	1061.2	990.5	936.3	943.3	905.7
1171.4	1165.8	1157.7	1147.9	1146.1	1139.0	996.8	986.5	949.3	922.2
1251.8	1206.9	1215.4	1227.8	1188.3	1205.2	1089.1	1031.0	956.2	956.7
1305.8	1228.5	1262.0	1275.4	1214.9	1233.0	1105.4	1086.1	975.1	1016.1
1365.8	1281.0	1301.0	1334.3	1261.6	1293.2	1111.2	1110.4	1067.8	1087.0
1370.3	1305.8	1356.5	1343.5	1285.0	1332.0	1171.7	1173.8	1129.9	1100.4
1420.4	1332.6	1389.9	1387.5	1328.0	1357.4	1228.2	1183.1	1161.7	1154.9
1452.4	1386.5	1465.9	1420.6	1356.1	1421.5	1276.7	1217.6	1183.5	1200.4
1473.8	1411.3	1531.6	1425.6	1383.3	1493.8	1296.1	1281.6	1262.5	1300.1
1477.8	1422.7	1555.6	1430.9	1405.6	1510.1	1343.3	1290.3	1353.0	1330.3
1546.2	1516.4	1563.5	1498.4	1477.3	1518.9	1355.8	1335.4	1387.6	1367.6
1560.5	1541.0	1568.5	1514.3	1492.7	1527.2	1378.8	1366.5	1430.6	1425.4
1565.9	1548.5	1572.7	1521.2	1505.6	1550.0	1439.2	1406.3	1449.0	1437.9
1574.1	1559.9	1754.9	1528.1	1516.3	1742.9	1458.4	1413.1	1466.0	1472.3
3022.1	1622.9	2957.8	2993.9	1612.7	2912.7	1473.5	1428.8	1526.4	1482.3
3078.7	3040.6	3018.5	3053.1	3016.3	2968.1	1544.5	1452.3	1538.4	1499.6
3092.7	3095.5	3107.9	3066.5	3071.4	3074.8	1553.2	1516.2	1541.6	1534.8
3098.5	3102.6	3121.3	3069.4	3075.2	3094.6	1560.2	1537.3	1555.0	1558.4
3102.9	3114.1	3183.4	3073.0	3087.5	3151.2	1561.0	1546.9	1563.7	1564.6
3143.6	3149.1	3187.5	3116.3	3122.4	3155.3	1565.9	1553.2	1570.5	1570.9
3163.0	3161.0	3200.8	3135.0	3128.1	3168.3	1574.2	1563.2	1717.1	1698.4
3191.5	3171.8	3205.3	3159.5	3147.5	3174.5	2994.7	1622.3	2930.4	2928.4
3194.2	3247.8	3296.6	3162.4	3211.9	3264.4	3086.0	3019.5	3106.4	3100.4
						3098.5	3094.6	3109.8	3103.4
						3101.9	3100.7	3121.5	3108.0
						3112.2	3110.1	3180.4	3160.9
						3138.2	3147.5	3188.1	3177.8
						3166.3	3159.8	3198.7	3183.0
						3191.3	3163.1	3199.4	3194.7
						3192.9	3203.6	3205.5	3196.0
						3204.3	3216.5	3231.2	3353.6
						3217.5	3246.3	3290.5	3370.6

III. (Free and hindered) internal rotors, (B/cm^{-1}, V$_0$/kcal mol^{-1}, Symmetrynumbers)

[a]: C_2H_5O—C_2H_5:	Mol/6-31:	4.507 , 5.69 , 1	[d]: C_3H_6O—C_2H_5:	Mol:	3.491 , 5.66 , 1
	Dec1/6-31:	4.367 , 3.40 , 1		Dec1:	3.491 , 3.68 , 1
	Mol/6-311:	4.508 , 4.80 , 1		Dec2:	3.460 , 8.65 , 1
	Dec1/6-311	4.372 , 2.48 , 1			
			[e]: C_3H_4O—C_3H_7:	Mol:	1.594 , 25.3 , 1
[b]: CH_2O—C_3H_7:	Mol/6-31:	8.459 , 7.82 , 1		Dec1	1.876 , 13.0 , 1
	Dec1/6-31:	10.42 , 3.87 , 1		Dec2	1.553 , 13.7 , 1
	Mol/6-311:	8.486 , 7.74 , 1			
	Dec1/6-311	10.38 , 3.89 , 1	[f]: C_4H_8O—CH_3:	Mol:	5.638 , 3.18 , 3
				Dec1:	5.664 , 2.47 , 3
[c]: C_3H_6O—CH_3:	Mol/6-31:	5.789 , 3.80 , 3		Dec2:	5.340 , 1.76 , 3
	Dec1/6-31:	5.760 , 3.71 , 3		Isom:	5.512 , 3.56 , 3
	Mol/6-311:	5.777 , 3.47 , 3			
	Dec1/6-311	5.746 , 3.52 , 3	[g]: C_4H_8O—‘CH_3:	Mol:	5.637 , 3.86 , 3
				Dec1:	5.621 , 3.79 , 3
				Dec2:	5.626 , 3.79 , 3

IV. Energy ranges

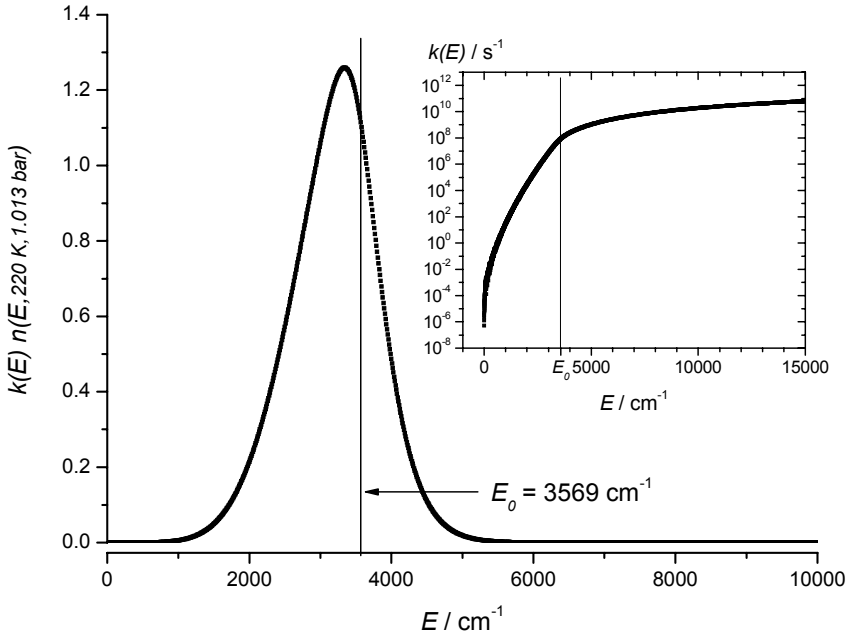
The question of the energy range below the threshold to be considered cannot be answered in general since this depends on the temperature and pressure via the actual population of the reactant ensemble *n(E)* as well as the energyspecific rate constants *k(E)* which are in addition most sensitive to the shape and the absolute height of the barrier. Nevertheless, we rationalise the calculation of the isomerisation rate coefficient of 1-butoxyl to show its dependence on the energy ranges considered for the final integration <*k(E)*> at *T*=220 K and *p*=1.013 bar. The following integral has been solved for different lower limits.

$$k(p) = \int_0^\infty k(E)n(E)dE \quad when \quad \int_0^\infty n(E)dE = 1$$

In practical an upper limit of 16950 cm^{-1} has been chosen and is sufficient large to represent +infinity at this temperature.

(Note: For higher temperatures higher upper limits had to be chosen to guarantee convergence of the integral.)

The figure below shows the product of *k(E) n(E)* from the actual tunnelling calculation for the isomerisation of 1-butoxyl. The *n(E)* has been obtained and normalised from the solution of the master equation at T=220 K and p =1.013 bar and corresponds to the largest eigenvalue. The *k(E)* as calculated from RRKM theory via the Eckart tunnelling probabilties are explicitly shown in the insert.



The final rate coefficient *k*(220K, 1.013 bar) corresponds to the area underneath the *k(E)n(E)* product function. Its convergence with respect to the lower limit of integration is shown below:

Lower limit (absolute energy interval)	Rate coefficient	Relative deviation
E_0 – 10 kJ/mol (2733 to 16950 cm^{-1})	1436.7 s^{-1}	-22.4%
E_0 – 15 kJ/mol (2315 to 16950 cm^{-1})	1686.4 s^{-1}	-8.9%
E_0 – 20 kJ/mol (1897 to 16950 cm^{-1})	1800.5 s^{-1}	-2.8%
E_0 – 25 kJ/mol (1479 to 16950 cm^{-1})	1841.1 s^{-1}	-0.6%
E_0 – 30 kJ/mol (1061 to 16950 cm^{-1})	1850.5 s^{-1}	-0.1%
E_0 – 35 kJ/mol (643 to 16950 cm^{-1})	1851.7 s^{-1}	-0.0%
Full (0 to 16950 cm^{-1})	1851.8 s^{-1}	exact

It is obvious that a potential function which resembles the true MEP up to 20-25 kJ/mol underneath the barrier can give an accurate representation of tunnelling effects and the corresponding enhanced rate coefficients. Although Eckart barriers often tend to become to small far down from the top, no significant errors would be introduced in this case, since the contributions for the low energies already became negligible (even for an eventually too small barrier).

V. Kinetic results: Rate expressions

Rate expressions are given in modified Arrhenius form when it is essentially necessary to reproduce the curvature of the calculated rates. (Positive exponents of the T^n term are due to tunnelling, negative exponents occur in general when away from the high pressure limit). The general accuracy is within a few percent for the temperature ranges given.

Extrapolations outside these limits are not recommended since additional effects must be taken into account such as non-stationary behaviour of the reacting molecule ensemble at higher temperatures which will make the definition of a rate coefficient apart from the theoretical high pressure limit obsolete!! (This is indeed the case as becomes visible by the lowering of the upper temperature limits with decreasing pressure. The ranges imposed guarantee thermal behaviour of all reaction channels.)

1-butoxyl (StandardMEP, MP2(full)/6-31G(d) geometries & frequencies, 3 hindered rotors)

-> δ-hydoxy-butyl (l=1.74 amu$^{0.5}$Å, E_0= 42.7 kJ/mol):

p -> ∞:	k_{iso}= 1.196 10^{11} (T/300K)$^{+1.412}$ exp(-3859.0 K/ T) s^{-1}	200 ≤ T ≤ 1200 K
p = 1013 mbar:	k_{iso}= 1.583 10^{12} (T/300K)$^{-2.303}$ exp(-4679.4 K/ T) s^{-1}	200 ≤ T ≤ 1100 K
p = 267 mbar:	k_{iso}= 1.016 10^{12} (T/300K)$^{-2.783}$ exp(-4617.8 K/ T) s^{-1}	200 ≤ T ≤ 1000 K

-> CH_2O + C_3H_7 (E_0= 62.8 kJ/mol):

p -> ∞:	k_{dec} = 9.503 10^{13} exp(-8081.4 K/ T) s^{-1}	200 ≤ T ≤ 1200 K
p = 1013 mbar:	k_{dec} = 7.926 10^{13} (T/300K)$^{-4.363}$ exp(-8445.5 K/ T) s^{-1}	200 ≤ T ≤ 1100 K
p = 267 mbar:	k_{dec} = 2.491 10^{12} (T/300K)$^{-3.611}$ exp(-7875.6 K/ T) s^{-1}	200 ≤ T ≤ 1000 K

2-pentoxyl (StandardMEP, MP2(full)/6-31G(d) geometries & frequencies, 4 hindered rotors)

-> δ-hydoxy-pentyl (l=1.91 amu$^{0.5}$Å, E_0= 40.2 kJ/mol):

p -> ∞:	k_{iso}= 1.364 10^{11} (T/300K)$^{+1.518}$ exp(-3683.1 K/ T) s^{-1}	200 ≤ T ≤ 1000 K
p = 1013 mbar:	k_{iso}= 4.650 10^{12} (T/300K)$^{-3.220}$ exp(-4781.6 K/ T) s^{-1}	200 ≤ T ≤ 1000 K
p = 267 mbar:	k_{iso}= 3.346 10^{12} (T/300K)$^{-3.713}$ exp(-4745.3 K/ T) s^{-1}	200 ≤ T ≤ 900 K

-> CH_3CHO + C_3H_7 (E_0= 50.7 kJ/mol):

p -> ∞:	k_{dec1}= 9.121 10^{13} exp(-6612.0 K/ T) s^{-1}	200 ≤ T ≤ 1000 K
p = 1013 mbar:	k_{dec1}= 7.684 10^{14} (T/300K)$^{-5.549}$ exp(-7474.9 K/ T) s^{-1}	200 ≤ T ≤ 1000 K
p = 267 mbar:	k_{dec1}= 1.438 10^{14} (T/300K)$^{-5.694}$ exp(-7195.0 K/ T) s^{-1}	200 ≤ T ≤ 900 K

-> C_3H_7CHO + CH_3 (E_0= 61.4 kJ/mol):

p -> ∞:	k_{dec2}= 8.159 10^{13} exp(-7905.1 K/ T) s^{-1}	200 ≤ T ≤ 1000 K
p = 1013 mbar:	k_{dec2}= 2.201 10^{14} (T/300K)$^{-5.995}$ exp(-8615.5 K/ T) s^{-1}	200 ≤ T ≤ 1000 K
p = 267 mbar:	k_{dec2}= 1.083 10^{13} (T/300K)$^{-5.493}$ exp(-8108.8 K/ T) s^{-1}	200 ≤ T ≤ 900 K

Additional results at arbitrary pressures and temperatures are available on request.