Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information to the paper

Impact of tunneling on hydrogen-migration of n-propyl peroxy radical

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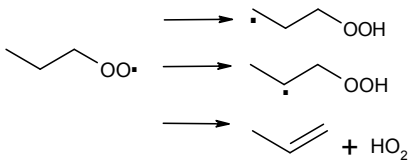
R1, R2, and R3 are given below for reference



1, 5 H-migration (R1)

1, 4 H-migration (R2)

HO_2 elimination (R3)

Table S1. Cartesian coordinates (in Å) of all stationary points for R1 to R3 at M05-2X/6-311+G(2df,2p) level

1-propyl peroxy radical			
C	0.965904	0.389142	0.575471
C	1.795034	-0.615443	-0.214444
H	2.198842	-0.160064	-1.116387
H	2.626691	-0.982206	0.379590
H	1.188731	-1.467151	-0.509443
H	0.575764	-0.062795	1.484428
H	1.579039	1.237663	0.875211
C	-0.200513	0.928405	-0.221268
O	-1.108006	-0.140645	-0.587065
H	-0.780735	1.657526	0.334846
H	0.113909	1.342142	-1.175003
O	-1.750093	-0.581573	0.448090

Product of R1			
C	1.616843	0.931677	0.065266
H	2.651223	1.226075	0.099258
H	-2.266940	0.850314	0.455493
C	1.257813	-0.483395	-0.199077
H	2.030649	-1.142000	0.199071
H	1.222223	-0.679700	-1.277384
C	-0.078261	-0.935519	0.373182
H	-0.173429	-2.014931	0.277227
H	-0.180220	-0.658130	1.421004
O	-1.200955	-0.450535	-0.350103
O	-1.414320	0.906506	0.013847
H	0.860325	1.694036	0.079152

Product of R2			
C	2.078955	-0.602935	0.105276
H	3.144916	-0.401227	0.045509
H	1.850765	-1.001942	1.092758
H	1.856475	-1.397043	-0.613786
C	1.272583	0.607866	-0.175646
H	1.631402	1.340040	-0.878819
C	-0.121833	0.697626	0.303322
H	-0.560136	1.676756	0.130871
H	-0.193487	0.450757	1.365176
O	-0.881546	-0.279258	-0.429383
O	-2.218301	-0.201217	0.047979
H	-2.309390	-1.038880	0.511804

TS of R1			
C	-1.318178	-0.857724	0.026071
H	-1.601806	-1.183236	1.018583
H	-0.021030	-1.246263	-0.009640
C	-1.132894	0.619360	-0.162089
H	-1.872167	1.184844	0.407200
H	-1.232170	0.888261	-1.209318
C	0.263714	1.048935	0.311549
H	0.477233	2.078526	0.042922
H	0.380926	0.904376	1.383941
O	1.217617	0.262498	-0.371694
O	1.131614	-1.023265	0.132332
H	-1.800689	-1.403801	-0.771975

TS of R2			
H	-0.158075	-0.826789	0.724714
C	0.770781	0.110213	0.638220
H	1.139709	0.327527	1.632365
C	-0.319728	1.029312	0.101298
H	-0.879789	1.485571	0.914736
H	0.036920	1.785472	-0.594389
O	-1.152237	0.145176	-0.635203
O	-1.319551	-0.919885	0.245679
C	1.793233	-0.344417	-0.358102
H	2.391947	-1.164177	0.026878
H	1.307735	-0.658947	-1.278395
H	2.470140	0.478363	-0.598208

TS of R3			
C	1.921909	-0.502272	-0.304741
C	0.866301	0.203000	0.524021
C	0.084376	1.200374	-0.026286
O	-1.677480	0.158631	-0.323763
O	-1.373831	-0.950898	0.172319
H	2.092480	-1.515635	0.047679
H	2.870920	0.027231	-0.266206
H	1.609073	-0.559396	-1.344655
H	1.052152	0.262997	1.589173
H	-0.178940	-0.647348	0.512325
H	-0.413903	1.927760	0.592572
H	0.143195	1.435910	-1.077298

Table S2. Barrier heights E_0 and reaction energies E_{rxn} (in kcal/mol) for R1 to R3 (including zero point energy correction)

method	R1			R2			R3		
	E_0	E_{rxn}	MUE	E_0	E_{rxn}	MUE	E_0	E_{rxn}	MUE
CCSD(T)/ maug-cc-PVTZ	24.68	16.10	0.00	33.25	13.92	0.00	30.07	16.81	0.00
CBS-QB3	23.80	15.90	0.54	32.10	13.75	0.66	30.90	18.20	1.11
B1B95/MG3S	24.59	20.02	2.01	32.75	16.52	1.56	29.07	16.21	0.80
B3LYP/ 6-31+G(d,p)	24.4	19.49	1.83	32.87	15.41	0.93	35.22	19.28	3.81
B3LYP/MG3S	24.47	18.75	1.43	33.04	14.61	0.45	26.91	14.10	2.93
B3PW91/MG3S	23.17	18.74	2.08	31.53	14.79	1.30	26.76	16.34	1.89
B98/MG3S	--	--	--	--	--	--	27.97	16.51	1.20
BMK/MG3S	26.72	18.68	2.31	36.09	16.52	2.72	35.22	19.28	3.81
CAM-B3LYP/ MG3S	26.12	18.68	2.01	34.79	15.1	1.36	31.88	17.67	1.34
M052x/ 6-31+G(2df,2p)	25.24	17.69	1.08	34.78	15.18	1.40	33.87	20.04	3.52
M052x/ 6-31+G(d,p)	25.67	18.33	1.61	34.92	15.23	1.49	34.27	20.91	4.15
M052x/ 6-311+G(2d,2p)	25.36	17.40	0.99	35.07	14.95	1.42	33.65	19.04	2.91
M052x/ 6-311+G(d,p)	25.62	17.48	1.16	35.28	14.94	1.53	33.88	19.83	3.42
M052X/MG3S	25.35	17.35	0.96	35.06	14.43	1.16	33.92	19.27	3.16
M062x/ 6-31+G(d,p)	26.07	17.63	1.46	35.56	15.15	1.77	34.67	21.39	4.59
M062x/MG3S	25.87	17.01	1.05	35.3	14.36	1.24	34.31	19.58	3.51
MPW3PBE/MG3S	22.69	18.64	2.27	31.19	14.87	1.51	26.76	17.90	2.20
ωB97XD/MG3S	26.44	19.29	2.48	35.11	16.36	2.15	31.47	18.89	1.74

MG3S = 6-311+G(2df,2p)

Table S-3. Multi-dimensional tunneling corrections of 1,5 H-migration based on the reaction path of -0.5 ~ 0.5 Å at M05-2X/6-31+G(d,p)

T(K)	ZCT	SCT	LCT	μOMT
300	7.96	31.25	11.59	31.25
400	3.31	6.43	4.12	6.43
500	2.19	3.27	2.51	3.27
600	1.74	2.28	1.90	2.28
700	1.51	1.84	1.61	1.84
800	1.37	1.59	1.44	1.59
900	1.28	1.45	1.33	1.45
1000	1.22	1.35	1.26	1.35

Figure S-1 Potential energy curves of R1 (1,5 H-migration) different approximations

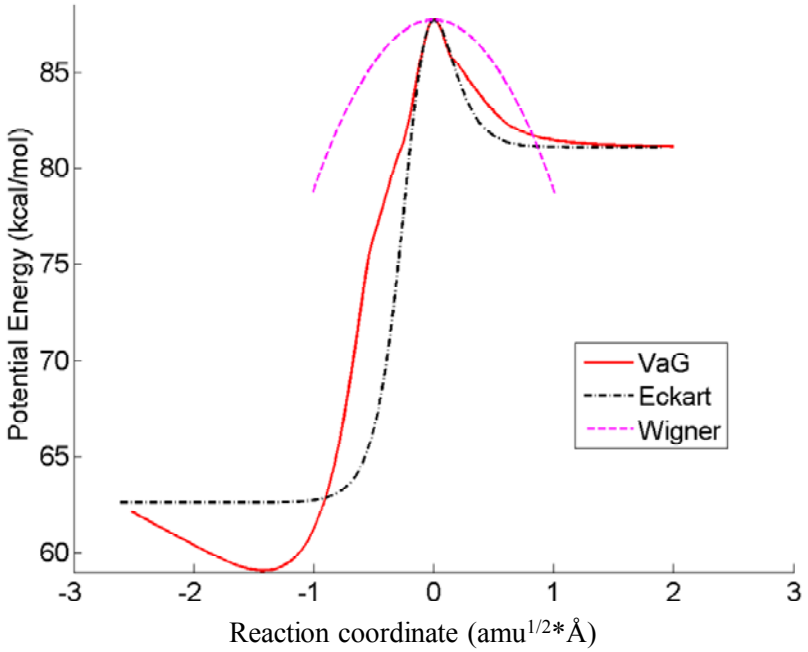


Table S-4. Transmission coefficients computed by different approximations for R1

E(kcal/mol)	ZCT	SCT	E(kcal/mol)	Eckart
81.10	1.76E-07	1.14E-05	81.10	--
81.17	2.38E-07	1.44E-05	81.18	5.76E-06
81.27	3.61E-07	1.99E-05	81.26	1.03E-05
81.32	4.29E-07	2.28E-05	81.33	1.57E-05
81.42	6.39E-07	3.10E-05	81.41	2.23E-05
81.48	7.97E-07	3.68E-05	81.49	3.04E-05
81.60	1.29E-06	5.36E-05	81.57	4.04E-05
81.67	1.68E-06	6.55E-05	81.65	5.26E-05
81.75	2.21E-06	8.08E-05	81.73	6.73E-05
81.83	2.93E-06	1.00E-04	81.81	8.50E-05
81.91	3.93E-06	1.26E-04	81.89	1.06E-04
82.00	5.32E-06	1.58E-04	81.97	1.31E-04
82.08	7.25E-06	2.00E-04	82.05	1.61E-04
82.18	9.95E-06	2.53E-04	82.21	2.39E-04
82.27	1.37E-05	3.23E-04	82.29	2.88E-04
82.37	1.91E-05	4.12E-04	82.37	3.45E-04
82.48	2.66E-05	5.28E-04	82.45	4.12E-04
82.58	3.73E-05	6.78E-04	82.61	5.80E-04
82.69	5.25E-05	8.71E-04	82.69	6.84E-04
82.80	7.40E-05	1.12E-03	82.84	9.43E-04
82.91	1.05E-04	1.44E-03	82.92	1.10E-03
83.03	1.48E-04	1.86E-03	83.00	1.29E-03
83.15	2.09E-04	2.39E-03	83.16	1.74E-03
83.27	2.95E-04	3.06E-03	83.24	2.01E-03
83.39	4.14E-04	3.91E-03	83.40	2.68E-03
83.51	5.81E-04	4.98E-03	83.56	3.53E-03
83.63	8.11E-04	6.32E-03	83.64	4.05E-03
83.76	1.13E-03	7.99E-03	83.72	4.64E-03
83.88	1.56E-03	1.01E-02	83.88	6.04E-03
84.01	2.16E-03	1.26E-02	84.04	7.83E-03
84.14	2.96E-03	1.57E-02	84.12	8.89E-03
84.27	4.03E-03	1.95E-02	84.28	1.14E-02
84.39	5.44E-03	2.40E-02	84.35	1.29E-02
84.52	7.30E-03	2.94E-02	84.51	1.64E-02
84.65	9.72E-03	3.57E-02	84.67	2.08E-02
84.78	1.28E-02	4.31E-02	84.75	2.34E-02
84.90	1.68E-02	5.13E-02	84.91	2.94E-02
85.03	2.19E-02	6.01E-02	84.99	3.30E-02
85.15	2.83E-02	6.93E-02	85.15	4.11E-02
85.28	3.63E-02	7.89E-02	85.31	5.10E-02
85.40	4.60E-02	8.89E-02	85.39	5.68E-02
85.52	5.79E-02	9.97E-02	85.55	6.99E-02

85.64	7.14E-02	1.11E-01	85.63	7.73E-02
85.76	8.49E-02	1.24E-01	85.79	9.43E-02
85.87	9.90E-02	1.37E-01	85.86	1.04E-01
85.99	1.14E-01	1.51E-01	86.02	1.26E-01
86.10	1.30E-01	1.66E-01	86.10	1.38E-01
86.21	1.47E-01	1.81E-01	86.18	1.51E-01
86.31	1.64E-01	1.97E-01	86.34	1.79E-01
86.41	1.83E-01	2.13E-01	86.42	1.95E-01
86.51	2.01E-01	2.30E-01	86.50	2.12E-01
86.61	2.21E-01	2.47E-01	86.58	2.29E-01
86.70	2.40E-01	2.65E-01	86.74	2.67E-01
86.79	2.60E-01	2.83E-01	86.82	2.87E-01
86.88	2.80E-01	3.01E-01	86.90	3.08E-01
86.96	3.00E-01	3.18E-01	86.98	3.29E-01
87.04	3.20E-01	3.36E-01	87.06	3.51E-01
87.11	3.40E-01	3.53E-01	87.14	3.74E-01
87.25	3.76E-01	3.86E-01	87.22	3.97E-01
87.31	3.93E-01	4.01E-01	87.30	4.21E-01
87.37	4.09E-01	4.16E-01	87.37	4.45E-01
87.47	4.37E-01	4.41E-01	87.45	4.69E-01
87.52	4.50E-01	4.53E-01	87.53	4.93E-01
87.62	4.79E-01	4.80E-01	87.61	5.17E-01
87.69	5.00E-01	5.00E-01	87.69	5.40E-01

Table S-5. Transmission coefficients computed by different approximations for R2

E(kcal/mol)	ZCT	SCT	E(kcal/mol)	Eckart
77.28	2.78E-23	2.80E-19	77.28	--
77.49	5.53E-22	5.10E-18	77.50	5.40E-13
77.67	3.86E-21	3.14E-17	77.72	1.65E-12
77.90	3.09E-20	2.24E-16	77.94	4.00E-12
78.18	2.65E-19	1.59E-15	78.17	8.61E-12
78.34	7.84E-19	4.32E-15	78.39	1.72E-11
78.51	2.34E-18	1.16E-14	78.61	3.25E-11
78.70	6.99E-18	3.07E-14	78.83	5.89E-11
78.89	2.09E-17	8.25E-14	79.05	1.03E-10
79.10	6.27E-17	2.17E-13	79.27	1.77E-10
79.32	1.87E-16	5.65E-13	79.49	2.95E-10
79.55	5.56E-16	1.47E-12	79.72	4.84E-10
79.79	1.65E-15	3.75E-12	79.94	7.80E-10
80.04	4.84E-15	9.49E-12	80.16	1.24E-09
80.30	1.42E-14	2.36E-11	80.38	1.94E-09
80.56	4.11E-14	5.76E-11	80.60	3.00E-09
80.84	1.19E-13	1.39E-10	80.82	4.59E-09
81.13	3.40E-13	3.28E-10	81.04	6.96E-09
81.42	9.64E-13	7.63E-10	81.49	1.56E-08
81.72	2.71E-12	1.75E-09	81.71	2.30E-08
82.03	7.57E-12	3.92E-09	81.93	3.38E-08
82.35	2.09E-11	8.67E-09	82.37	7.13E-08
82.67	5.72E-11	1.88E-08	82.60	1.03E-07
83.00	1.55E-10	4.03E-08	83.04	2.09E-07
83.33	4.13E-10	8.46E-08	83.26	2.96E-07
83.67	1.09E-09	1.75E-07	83.70	5.87E-07
84.01	2.83E-09	3.56E-07	83.92	8.20E-07
84.35	7.23E-09	7.12E-07	84.37	1.58E-06
84.70	1.82E-08	1.40E-06	84.59	2.18E-06
85.05	4.51E-08	2.73E-06	85.03	4.11E-06
85.41	1.10E-07	5.22E-06	85.47	7.65E-06
85.76	2.65E-07	9.87E-06	85.70	1.04E-05
86.12	6.27E-07	1.84E-05	86.14	1.90E-05
86.48	1.47E-06	3.38E-05	86.36	2.55E-05
86.83	3.34E-06	6.07E-05	86.80	4.58E-05
87.19	7.35E-06	1.06E-04	87.25	8.13E-05
87.54	1.57E-05	1.78E-04	87.47	1.08E-04
87.90	3.24E-05	2.94E-04	87.91	1.89E-04
88.25	6.51E-05	4.73E-04	88.13	2.49E-04
88.60	1.27E-04	7.45E-04	88.35	3.28E-04
88.94	2.41E-04	1.14E-03	88.57	4.31E-04
89.28	4.48E-04	1.69E-03	88.80	5.65E-04

89.62	8.11E-04	2.44E-03	89.02	7.39E-04
89.95	1.40E-03	3.48E-03	89.24	9.64E-04
90.28	2.27E-03	4.90E-03	89.46	1.26E-03
90.60	3.53E-03	6.83E-03	89.68	1.63E-03
90.92	5.30E-03	9.42E-03	89.90	2.12E-03
91.23	7.78E-03	1.29E-02	90.12	2.74E-03
91.53	1.12E-02	1.74E-02	90.35	3.54E-03
91.82	1.58E-02	2.33E-02	90.57	4.57E-03
92.11	2.18E-02	3.07E-02	90.79	5.89E-03
92.39	2.96E-02	4.00E-02	91.01	7.56E-03
92.66	3.96E-02	5.16E-02	91.23	9.70E-03
92.91	5.21E-02	6.57E-02	91.45	1.24E-02
93.16	6.75E-02	8.25E-02	91.68	1.58E-02
93.40	8.60E-02	1.02E-01	91.90	2.02E-02
93.63	1.08E-01	1.25E-01	92.12	2.56E-02
93.85	1.32E-01	1.50E-01	92.34	3.24E-02
94.06	1.60E-01	1.78E-01	92.56	4.09E-02
94.26	1.89E-01	2.07E-01	92.78	5.15E-02
94.44	2.21E-01	2.38E-01	93.00	6.45E-02
94.61	2.53E-01	2.69E-01	93.23	8.04E-02
94.77	2.86E-01	3.01E-01	93.45	9.97E-02
95.05	3.48E-01	3.60E-01	93.89	1.50E-01
95.18	3.77E-01	3.87E-01	94.11	1.83E-01
95.29	4.03E-01	4.11E-01	94.33	2.20E-01
95.38	4.27E-01	4.33E-01	94.55	2.62E-01
95.46	4.48E-01	4.52E-01	94.78	3.08E-01
95.59	4.79E-01	4.80E-01	95.22	4.12E-01
95.66	4.96E-01	4.96E-01	95.66	5.24E-01

Table S6. Tunneling coefficients computed by different approximations for R1 at M05-2X/MG3S

T(K)	Wigner	Eckart	ZCT	SCT
200	8.27	1.40×10^{3}	1.91×10^{2}	1.60×10^{3}
250	5.66	1.12×10^{2}	3.10×10^{1}	1.48×10^{2}
300	4.23	2.62×10^{1}	1.13×10^{1}	3.54×10^{1}
400	2.82	6.12	4.06	7.82
500	2.16	3.17	2.49	3.90
600	1.81	2.23	1.89	2.59
700	1.59	1.81	1.60	2.02
800	1.45	1.59	1.44	1.71
900	1.36	1.45	1.33	1.53
1000	1.29	1.35	1.26	1.41
1100	1.24	1.29	1.21	1.33
1200	1.20	1.24	1.18	1.27
1300	1.17	1.20	1.15	1.23
1400	1.15	1.18	1.13	1.19
1500	1.13	1.15	1.11	1.17

Table S7. Tunneling coefficients computed by different approximations for R2 at B3LYP/MG3S

T(K)	Wigner	Eckart	ZCT	SCT
300	5.52	3906	176	1684
400	3.54	41.85	15.40	45.58
500	2.63	7.83	5.29	9.39
600	2.13	3.76	3.06	4.29
700	1.83	2.55	2.23	2.78
800	1.64	2.02	1.83	2.14
900	1.50	1.73	1.60	1.80
1000	1.41	1.56	1.46	1.60
1100	1.34	1.44	1.36	1.47
1200	1.28	1.36	1.29	1.37
1300	1.24	1.30	1.24	1.31
1400	1.21	1.26	1.21	1.26
1500	1.18	1.22	1.18	1.22

Table S8. High pressure limit rate constants (sec^{-1}) by CVT/SCT for R1 to R3

T(K)	R1	R2	R3
500	1.14×10^{1}	1.69×10^{-2}	2.94×10^{-1}
600	5.80×10^{2}	2.27×10^{0}	4.35×10^{1}
700	1.03×10^{4}	8.79×10^{1}	1.60×10^{3}
800	9.39×10^{4}	1.48×10^{3}	2.47×10^{4}
900	5.43×10^{5}	1.40×10^{4}	2.11×10^{5}
100	2.27×10^{6}	8.77×10^{4}	1.19×10^{6}
110	7.47×10^{6}	4.02 x 105	4.95×10^{6}
1200	2.05×10^{7}	1.45×10^{6}	1.64×10^{7}
1300	4.90×10^{7}	4.38×10^{6}	4.57×10^{7}
1400	1.04×10^{8}	1.14×10^{7}	1.10×10^{8}
1500	2.03×10^{8}	2.62×10^{7}	2.39×10^{8}
1600	3.66×10^{8}	5.50×10^{7}	4.71×10^{8}
1700	6.21×10^{8}	1.06×10^{8}	8.62×10^{8}
1800	9.99×10^{8}	1.92×10^{8}	1.48×10^{9}
1900	1.54×10^{9}	3.26×10^{8}	2.41×10^{9}
2000	2.27×10^{9}	5.29×10^{8}	3.74×10^{9}