SUPPORTING INFORMATION

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Path-dependent variational effects and multidimensional tunneling in multi-path variational transition state theory: rate constants calculated for the reactions of HO_2 with *tert*-butanol by including all 46 paths for abstraction at C and all six paths for abstraction at O

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Table S1. Classical barrier height and energy of reaction (kcal/mol) computed by various model chemistries. Single point calculations were carried out based on the lowest–energy–structures optimized at M08–HX/MG3S level of theory.

	R1			R2		
Model chemistries	V_f	V_r	ΔE	V_f	V_r	ΔE
M05/MG3S	21.05	3.23	17.82	20.78	0.20	20.58
M05/ma-TZVP	22.39	3.37	19.02	21.34	0.52	20.82
M06-2X/MG3S	19.08	2.30	16.78	20.43	0.59	19.84
M06-2X/ma-TZVP	19.86	2.54	17.32	21.23	1.00	20.23
M08-HX/MG3S	20.58	3.47	17.11	23.05	2.51	20.54
M08-HX/ma-TZVP	21.95	3.85	18.10	24.18	3.16	21.02
M08-SO/MG3S	20.97	4.24	16.73	22.46	1.76	20.70
M08-SO/ma-TZVP	22.47	4.35	18.12	23.25	2.17	21.08
CCSD(T)-F12a/jun-cc-pVTZ	20.24	4.07	16.17	23.40	3.44	19.96

Table S2. $F_{act}^{MS\text{-}T}$ factors computed by M08–HX/MG3S at various temperatures (K) for forward and reverse reactions of R1 and R2

	R1		R2	
T/K	$F_{act,\,fwd}^{MS\text{-}T}$	$F_{act,\,rev}^{MS\text{-}T}$	$F_{act,\,fwd}^{MS\text{-}T}$	$F_{act,\,rev}^{MS\text{-}T}$
200	1.76	0.43	1.78	0.95
250	2.14	0.47	1.83	0.97
298.15	2.54	0.52	1.88	1.00
300	2.57	0.52	1.89	0.99
400	3.59	0.65	2.04	1.05
500	4.77	0.80	2.19	1.10
600	6.01	0.96	2.33	1.14
800	8.56	1.30	2.57	1.22
1000	10.92	1.64	2.75	1.27
1500	15.45	2.41	2.96	1.35
2000	18.33	3.02	3.01	1.36
2400	19.69	3.39	2.97	1.34

Table S3. MP–CVT/SCT rate constants ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) including all the paths for forward and reverse reactions of R1 and R2 at various temperatures (K)

	R1		R2	
T/K	$k_{fwd}^{MP\text{-}CVT/SCT}$	$k_{rev}^{MP\text{-}CVT/SCT}$	$k_{fwd}^{MP\text{-}CVT/SCT}$	$k_{rev}^{MP\text{-}CVT/SCT}$
200	4.85×10^{-33}	1.11×10^{-16}	1.02×10^{-36}	2.50×10^{-15}
250	1.96×10^{-29}	1.17×10^{-16}	3.26×10^{-32}	3.11×10^{-15}
298.15	4.87×10^{-27}	1.34×10^{-16}	2.86×10^{-29}	3.88×10^{-15}
300	5.85×10^{-27}	1.35×10^{-16}	3.58×10^{-29}	3.89×10^{-15}
400	1.01×10^{-23}	2.06×10^{-16}	2.74×10^{-25}	6.07×10^{-15}
500	$1.20\times10\text{-}^{21}$	3.35×10^{-16}	6.00×10^{-23}	7.88×10^{-15}
600	$3.55\times10\text{-}^{20}$	5.48×10^{-16}	2.76×10^{-21}	1.17×10^{-14}
800	3.46×10^{-18}	1.37×10^{-15}	4.25×10^{-19}	2.41×10^{-14}
1000	6.97×10^{-17}	3.03×10^{-15}	1.06×10^{-17}	4.44×10^{-14}
1500	6.00×10^{-15}	1.41×10^{-14}	1.13×10^{-15}	1.50×10^{-13}
2000	7.49×10^{-14}	4.24×10^{-14}	1.55×10^{-14}	3.64×10^{-13}
2400	2.96×10^{-13}	8.37×10^{-14}	6.38×10^{-14}	6.31×10^{-13}

Table S4. Fitting parameters for rate constants of R1 and R2 and overall reaction[a,b]

	ln A	n	T_0	E
R1, fwd	-38.239	5.776	88.432	11.120
R1, rev	-36.233	3.071	660.802	4.160
R2, fwd	-34.757	3.950	4.954	18.051
R2, rev	-36.292	3.774	166.432	-0.715
overall, fwd	-34.455	4.440	-11.694	16.139
overall, rev	-36.508	3.900	198.924	-0.715

[a] The rate constants are fitted using the following equations:

$$k = \begin{cases} A(\frac{T}{300})^n \exp[-\frac{E(T+T_0)}{R(T^2+T_0^2)}] & \text{endothermic forward reactions} \\ A(\frac{T+T_0}{300})^n \exp[-\frac{E(T+T_0)}{R(T^2+T_0^2)}] & \text{exothermic reverse reactions} \end{cases}$$

The Tolman activation energies (which may also be called temperature-dependent Arrhenius activation energies) are given by

$$E_a = \begin{cases} \frac{E(T^4+2T_0T^3-T_0^2T^2)}{(T^2+T_0^2)^2} + nRT & \text{endothermic reactions} \\ \frac{E(T^4+2T_0T^3-T_0^2T^2)}{(T^2+T_0^2)^2} + \frac{nRT^2}{T+T_0} & \text{exothermic reactions} \end{cases} \quad (1)$$

where E, T_0, and n are the fitting parameters.

[b] The unit of A is cm^3 $molecule^{-1}$ s^{-1}; the parameters T_0 and E are in units of K and kcal/mol respectively, and n is unitless. The overall reaction is the sum of reactions R1 and R2, but the sum is fit separately.

Table S5. Arrhenius Activation energies (kcal/mol) for forward reactions at various temperatures (K)

T/K	R1	R2	overall
200	15.44	20.48	15.86
250	16.77	20.71	16.74
298.15	17.56	20.98	17.43
300	17.59	20.99	17.46
400	18.67	21.63	18.69
500	19.57	22.33	19.77
600	20.45	23.05	20.79
800	22.30	24.55	22.72
1000	24.28	26.08	24.58
1500	29.52	29.94	29.12
2000	34.99	33.84	33.60
2400	39.44	36.96	37.16

Table S6. Phenomenological Gibbs free energies of activation (kcal/mol) for forward reactions at various temperatures (K)

T/K	R1	R2	overall
200	23.22	26.58	23.22
250	25.12	28.30	25.12
298.15	26.90	29.94	26.90
300	26.97	30.00	26.96
400	30.49	33.35	30.47
500	33.80	36.78	33.76
600	36.96	40.01	36.87
800	42.92	46.25	42.73
1000	48.57	52.32	48.29
1500	61.99	66.97	61.48
2000	74.91	81.16	74.16
2400	85.07	92.39	84.14

Table S7. Differences between SCT representative tunneling energies at 200 K, widths of the vibrationally adiabatic ground-state potential curves at the representative tunneling energies, and ratios of SCT tunneling transmission coefficients to the ZCT ones for various paths of reaction R1.

Path	$V_{a,p}^{AG} - E_{rep,p}(200\ K)$ (kcal/mol)	$s_> - s_<$ (Å)	$\kappa^{SCT}/\kappa^{ZCT}$ (200 K)
1	2.64	0.47	1.5
9	3.39	0.58	3.2
19	4.66	0.83	5.2
29	4.87	0.84	6.9
41	4.69	0.83	8.4
45	5.19	0.88	11.4

Table S8. Cartesian coordinates of lowest–energy–structures of reactants, products, and transition structures of R1 and R2 optimized at M08–HX/MG3S level

***tert*–butanol**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.006082	0.000000	0.019773
2	8	0	0.050068	−0.000013	1.444478
3	6	0	−1.487648	−0.000041	−0.326208
4	6	0	0.673507	1.255264	−0.522436
5	6	0	0.673583	−1.255213	−0.522459
6	1	0	0.968257	0.000002	1.720551
7	1	0	−1.629191	−0.000022	−1.410776
8	1	0	−1.971471	0.886836	0.092130
9	1	0	−1.971415	−0.886968	0.092090
10	1	0	0.608392	1.295969	−1.614155
11	1	0	1.734767	1.268754	−0.248056
12	1	0	0.198252	2.148970	−0.108667
13	1	0	0.608479	−1.295901	−1.614179
14	1	0	1.734842	−1.268645	−0.248072
15	1	0	0.198380	−2.148955	−0.108707

HO_2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.875517	-0.869527	0.000000
2	8	0	0.054720	-0.597182	0.000000
3	8	0	0.054720	0.705873	0.000000

H_2O_2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.019829	0.629889	0.460298
2	8	0	-0.700574	-0.114617	-0.057537
3	8	0	0.700574	0.114617	-0.057537
4	1	0	1.019830	-0.629889	0.460299

TS of R1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.417444	0.113184	0.358559
2	6	0	0.935928	-0.021661	0.010419
3	6	0	0.175869	1.131906	0.627656
4	8	0	0.509168	-1.244861	0.591195
5	6	0	0.736324	-0.057730	-1.504165
6	8	0	-2.192389	0.725037	-0.149055
7	8	0	-2.338951	-0.642687	0.051081
8	1	0	-0.409066	-1.388370	0.343118
9	1	0	2.834484	1.034033	-0.057902
10	1	0	2.960088	-0.741888	-0.055488
11	1	0	2.553202	0.117410	1.443204
12	1	0	1.071452	0.876112	-1.966239
13	1	0	-0.322208	-0.198465	-1.747363
14	1	0	1.309014	-0.885992	-1.929436
15	1	0	0.112364	1.103863	1.716161
16	1	0	0.392410	2.120180	0.218943
17	1	0	-1.101353	0.966891	0.248746
18	1	0	-2.816401	-0.697883	0.885665

TS of R2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.236565	-0.493620	-0.679379
2	6	0	-0.938564	-0.021920	0.009496
3	8	0	-0.042279	0.117508	-1.049607
4	6	0	-0.452215	-1.080622	0.998166
5	6	0	-1.165308	1.322947	0.698831
6	1	0	1.081318	0.478403	-0.650771
7	1	0	-3.008012	-0.619731	0.085994
8	1	0	-2.072416	-1.447568	-1.185258
9	1	0	-2.570753	0.247539	-1.408696
10	1	0	-1.207922	-1.255924	1.769751
11	1	0	0.471332	-0.749567	1.481866
12	1	0	-0.251497	-2.021084	0.477709
13	1	0	-1.910366	1.227114	1.494196
14	1	0	-0.227647	1.673133	1.141928
15	1	0	-1.512109	2.066035	-0.024214
16	8	0	2.013988	0.714652	-0.111252
17	8	0	2.633992	-0.496290	0.084598
18	1	0	3.118375	-0.646011	-0.735093

Table S8. Coordinates and energies of all optimized structures

For each reactant, product, and transition state we give the structures, potential energies (V, relative to the lowest-energy conformer), and ground-state energies (V + ZPE) of all conformations as calculated by M08–HX/MG3S. The structures are in Å, and the energies are in kcal/mol. The zero-point energies (ZPEs) are calculated in the quasiharmonic approximation, that is, the harmonic approximation with scaled frequencies, as discussed in the text. For each reactant, product, and transition state, the conformations are numbered in order of increasing potential energy. When conformations occur in enantiomeric pairs, only one enantiomer is tabulated and so only structures with odd structure numbers occur in the table in those cases.

TS of R1

Conformer 1 potential energy: 0 kcal/mol ground-state energy: 89.7 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.417444	0.113184	0.358559
2	6	0	0.935928	−0.021661	0.010419
3	6	0	0.175869	1.131906	0.627656
4	8	0	0.509168	−1.244861	0.591195
5	6	0	0.736324	−0.057730	−1.504165
6	8	0	−2.192389	0.725037	−0.149055
7	8	0	−2.338951	−0.642687	0.051081
8	1	0	−0.409066	−1.388370	0.343118
9	1	0	2.834484	1.034033	−0.057902
10	1	0	2.960088	−0.741888	−0.055488
11	1	0	2.553202	0.117410	1.443204
12	1	0	1.071452	0.876112	−1.966239
13	1	0	−0.322208	−0.198465	−1.747363
14	1	0	1.309014	−0.885992	−1.929436
15	1	0	0.112364	1.103863	1.716161
16	1	0	0.392410	2.120180	0.218943
17	1	0	−1.101353	0.966891	0.248746
18	1	0	−2.816401	−0.697883	0.885665

Conformer 3 potential energy: 0.3 kcal/mol ground-state energy: 90.0 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.073865	1.336641	0.685630
2	6	0	0.909684	-0.009195	-0.015829
3	6	0	0.063524	0.127849	-1.253600
4	8	0	0.208055	-0.916934	0.843852
5	6	0	2.271827	-0.609052	-0.376438
6	8	0	-2.079352	0.703555	-0.115820
7	8	0	-2.498772	-0.598830	0.098698
8	1	0	0.716228	-1.037193	1.648278
9	1	0	1.569124	2.057764	0.028647
10	1	0	1.688163	1.224605	1.586048
11	1	0	0.094122	1.728336	0.971415
12	1	0	2.818503	0.048624	-1.057921
13	1	0	2.143003	-1.584575	-0.851921
14	1	0	2.877767	-0.737096	0.528649
15	1	0	0.396320	0.881740	-1.964940
16	1	0	-0.265993	-0.811774	-1.698487
17	1	0	-1.146112	0.577276	-0.773209
18	1	0	-1.843973	-0.927493	0.731020

Conformer 5 potential energy: 0.8 kcal/mol ground-state energy: 90.4 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.319594	-0.488208	0.361810
2	6	0	0.913506	-0.001579	0.002971
3	6	0	0.103280	0.217413	1.260127
4	8	0	0.269287	-0.981031	-0.822081
5	6	0	0.977813	1.267756	-0.834436
6	8	0	-2.101966	0.693384	0.173045
7	8	0	-2.478302	-0.604929	-0.127535
8	1	0	0.363030	-1.842808	-0.410118
9	1	0	2.848844	0.258521	0.960009
10	1	0	2.888810	-0.673684	-0.554200
11	1	0	2.274668	-1.416209	0.943058

12	1	0	1.445218	2.075284	−0.264003
13	1	0	−0.030051	1.577265	−1.122737
14	1	0	1.566322	1.087407	−1.737609
15	1	0	−0.154349	−0.683923	1.820200
16	1	0	0.408833	1.056801	1.884260
17	1	0	−1.141499	0.569210	0.790101
18	1	0	−1.867150	−0.839545	−0.839220

Conformer 7 potential energy: 0.8 kcal/mol ground-state energy: 90.5 kcal/mol

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	−2.422478	0.262605	−0.213336
2	6	0	−0.931981	−0.011750	−0.014979
3	6	0	−0.192190	1.302238	0.083911
4	8	0	−0.514278	−0.719613	−1.170628
5	6	0	−0.714951	−0.850931	1.245368
6	8	0	2.260295	0.695019	0.236272
7	8	0	2.317801	−0.572635	−0.331398
8	1	0	0.440832	−0.833973	−1.139091
9	1	0	−2.837836	0.807981	0.638341
10	1	0	−2.950486	−0.690293	−0.316733
11	1	0	−2.579270	0.845373	−1.124335
12	1	0	−1.113986	−0.340806	2.127587
13	1	0	0.351171	−1.030441	1.417975
14	1	0	−1.218480	−1.814863	1.136955
15	1	0	−0.197384	1.897416	−0.829948
16	1	0	−0.363943	1.879682	0.993316
17	1	0	1.114368	0.999537	0.186441
18	1	0	2.414071	−1.154755	0.429733

Conformer 9 potential energy: 0.9 kcal/mol ground-state energy: 90.5 kcal/mol

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	2.356891	0.360486	0.223011
2	6	0	0.889267	−0.003338	−0.013163

3	6	0	0.189214	1.125816	−0.738769
4	8	0	0.257806	−0.242073	1.253694
5	6	0	0.778553	−1.306758	−0.791779
6	8	0	−2.203028	0.717934	−0.081432
7	8	0	−2.272178	−0.654681	0.078639
8	1	0	0.306051	0.555389	1.785391
9	1	0	2.871045	0.539827	−0.725532
10	1	0	2.858347	−0.458240	0.747777
11	1	0	2.438744	1.268598	0.830396
12	1	0	1.308968	−1.218208	−1.744054
13	1	0	−0.267824	−1.547355	−0.995001
14	1	0	1.227338	−2.120456	−0.215844
15	1	0	0.294741	2.112844	−0.282870
16	1	0	0.291542	1.135298	−1.823147
17	1	0	−1.160030	0.911345	−0.514918
18	1	0	−1.713269	−0.805719	0.854791

Conformer 11 potential energy: 1.0 kcal/mol ground-state energy: 90.5 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.575433	1.483552	0.126127
2	6	0	0.983559	0.016643	0.004049
3	6	0	0.145207	−0.691269	−1.038176
4	8	0	0.833929	−0.641565	1.253574
5	6	0	2.461808	−0.107322	−0.358717
6	8	0	−2.011821	−0.662022	0.251149
7	8	0	−2.663524	0.510834	−0.100622
8	1	0	−0.090532	−0.587122	1.514284
9	1	0	0.728348	2.011914	−0.820249
10	1	0	1.179128	1.966638	0.898882
11	1	0	−0.481450	1.569724	0.398212
12	1	0	2.666470	0.363413	−1.324115
13	1	0	2.752943	−1.159824	−0.404576
14	1	0	3.062935	0.386309	0.410706
15	1	0	−0.023775	−0.160831	−1.976023
16	1	0	0.353427	−1.756120	−1.149836
17	1	0	−1.071509	−0.715183	−0.462904
18	1	0	−3.340698	0.213488	−0.716881

Conformer 13 potential energy: 1.0 kcal/mol ground-state energy: 91.0 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.050821	-1.033047	0.167548
2	6	0	0.919299	-0.022089	0.008487
3	6	0	0.030527	-0.045599	1.233635
4	8	0	0.174936	-0.443777	-1.140840
5	6	0	1.464436	1.381996	-0.231833
6	8	0	-2.036392	0.711386	0.094226
7	8	0	-2.532633	-0.571027	-0.083129
8	1	0	-0.362629	0.303110	-1.421598
9	1	0	2.650582	-0.805475	1.052914
10	1	0	2.695114	-1.004431	-0.715975
11	1	0	1.642033	-2.041761	0.268539
12	1	0	2.076810	1.712207	0.612095
13	1	0	0.640417	2.095445	-0.352331
14	1	0	2.077401	1.396112	-1.137046
15	1	0	-0.400902	-1.017829	1.479911
16	1	0	0.374875	0.527918	2.093403
17	1	0	-1.121550	0.541873	0.800607
18	1	0	-1.909931	-0.967380	-0.709596

Conformer 15 potential energy: 1.3 kcal/mol ground-state energy: 90.8 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.371698	0.331104	0.223684
2	6	0	0.892912	0.010656	-0.012918
3	6	0	0.172305	1.253738	-0.466763
4	8	0	0.289854	-0.363567	1.234247
5	6	0	0.742945	-1.117258	-1.031580
6	8	0	-2.252621	0.708812	-0.053682
7	8	0	-2.269781	-0.671425	0.051427
8	1	0	0.836524	-1.032074	1.651750
9	1	0	2.848307	0.672504	-0.699276
10	1	0	2.902149	-0.567591	0.562533
11	1	0	2.475472	1.109230	0.984387
12	1	0	1.208969	-0.837496	-1.981377

13	1	0	-0.313421	-1.335520	-1.205579
14	1	0	1.237708	-2.024116	-0.666972
15	1	0	0.236406	2.097973	0.219863
16	1	0	0.303755	1.514221	-1.515696
17	1	0	-1.175325	0.971520	-0.349746
18	1	0	-1.779319	-0.828645	0.869644

Conformer 17 potential energy: 2.2 kcal/mol ground-state energy: 91.6 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.594990	1.473367	0.189921
2	6	0	1.000979	0.012261	0.002760
3	6	0	0.109652	-0.672333	-1.007429
4	8	0	0.927523	-0.675036	1.243947
5	6	0	2.458223	-0.086270	-0.443112
6	8	0	-2.034294	-0.620484	0.301576
7	8	0	-2.818782	0.363242	-0.278941
8	1	0	0.013927	-0.668679	1.543796
9	1	0	0.644048	2.023730	-0.754406
10	1	0	1.258916	1.952013	0.914327
11	1	0	-0.428947	1.536140	0.574118
12	1	0	2.607312	0.422772	-1.399094
13	1	0	2.749808	-1.134247	-0.547277
14	1	0	3.099273	0.379586	0.311221
15	1	0	-0.102983	-0.126697	-1.927301
16	1	0	0.306178	-1.735867	-1.146205
17	1	0	-1.096258	-0.700337	-0.401170
18	1	0	-2.629915	1.147661	0.246493

Conformer 19 potential energy: 2.4 kcal/mol ground-state energy: 91.7 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.534587	-1.190659	-0.846330
2	6	0	-1.015135	-0.030734	0.017357
3	6	0	-0.061454	0.211438	1.168594

4	8	0	−2.303756	−0.317771	0.566542
5	6	0	−1.186423	1.233881	−0.809277
6	8	0	2.085859	0.736673	−0.035556
7	8	0	2.672679	−0.517621	−0.111901
8	1	0	−2.278740	−1.178527	0.989071
9	1	0	0.446981	−0.971478	−1.276635
10	1	0	−1.248378	−1.374393	−1.653947
11	1	0	−0.439771	−2.105009	−0.248424
12	1	0	−0.228916	1.530432	−1.246969
13	1	0	−1.559729	2.047570	−0.181146
14	1	0	−1.907281	1.057753	−1.611812
15	1	0	−0.305041	1.067207	1.798640
16	1	0	0.246158	−0.677451	1.724918
17	1	0	1.101097	0.555046	0.572081
18	1	0	3.320964	−0.504949	0.599484

Conformer 21 potential energy: 2.5 kcal/mol ground-state energy: 91.8 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.169625	−1.089198	−0.983776
2	6	0	−1.014720	0.047335	0.020291
3	6	0	−0.075004	−0.352694	1.138428
4	8	0	−2.279236	0.371810	0.603705
5	6	0	−0.529580	1.316791	−0.660524
6	8	0	2.088961	−0.740256	−0.093672
7	8	0	2.686336	0.510504	−0.069031
8	1	0	−2.684397	−0.429835	0.940413
9	1	0	−0.206185	−1.322566	−1.447348
10	1	0	−1.879981	−0.803710	−1.764235
11	1	0	−1.539174	−1.996336	−0.490604
12	1	0	0.458417	1.159638	−1.101678
13	1	0	−0.463438	2.130811	0.066655
14	1	0	−1.233590	1.608616	−1.444246
15	1	0	0.189812	0.447763	1.830562
16	1	0	−0.297814	−1.304040	1.626579
17	1	0	1.101490	−0.603037	0.516947
18	1	0	3.319937	0.442829	0.652428

Conformer 23 potential energy: 2.7 kcal/mol ground-state energy: 92.0 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.766313	1.424165	−0.531901
2	6	0	−0.981339	0.012052	−0.012307
3	6	0	−0.167206	−0.991676	−0.803140
4	8	0	−2.362611	−0.277959	−0.245186
5	6	0	−0.661992	−0.080825	1.475071
6	8	0	2.236230	−0.742414	−0.064245
7	8	0	2.429384	0.609707	0.175354
8	1	0	−2.588071	−1.101883	0.191413
9	1	0	0.277936	1.717706	−0.398328
10	1	0	−1.405137	2.121100	0.016901
11	1	0	−1.026641	1.479139	−1.592778
12	1	0	0.382292	0.186663	1.662017
13	1	0	−0.820856	−1.101485	1.843057
14	1	0	−1.310508	0.597493	2.036337
15	1	0	−0.304546	−2.032813	−0.501218
16	1	0	−0.170782	−0.851366	−1.884389
17	1	0	1.133249	−0.829289	−0.443423
18	1	0	2.870144	0.917762	−0.623312

Conformer 25 potential energy: 2.8 kcal/mol ground-state energy: 92.1 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.658353	0.130127	1.483681
2	6	0	−0.981456	0.000596	0.003513
3	6	0	−0.160862	0.976831	−0.814897
4	8	0	−2.356080	0.372078	−0.131744
5	6	0	−0.777265	−1.430749	−0.478380
6	8	0	2.235241	0.734580	−0.052287
7	8	0	2.429035	−0.624818	0.141107
8	1	0	−2.636505	0.212984	−1.035199
9	1	0	0.382000	−0.149489	1.671239
10	1	0	−1.316916	−0.523304	2.061942
11	1	0	−0.813727	1.160472	1.815282
12	1	0	0.266131	−1.730094	−0.345037
13	1	0	−1.031647	−1.522981	−1.541233

14	1	0	−1.417036	−2.109749	0.091806
15	1	0	−0.129669	0.793635	−1.891169
16	1	0	−0.323693	2.023642	−0.554911
17	1	0	1.133434	0.829822	−0.434739
18	1	0	2.889673	−0.900494	−0.658096

Conformer 27 potential energy: 3.0 kcal/mol ground-state energy: 92.3 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.357138	−1.121174	−0.891904
2	6	0	−1.011078	0.046464	0.025371
3	6	0	−0.040272	−0.388669	1.100322
4	8	0	−2.188952	0.550297	0.658682
5	6	0	−0.449234	1.212546	−0.776019
6	8	0	2.099585	−0.738545	−0.167087
7	8	0	2.761983	0.435245	0.151527
8	1	0	−2.616101	−0.161493	1.139464
9	1	0	−0.454698	−1.502181	−1.381022
10	1	0	−2.068278	−0.801054	−1.658085
11	1	0	−1.805950	−1.942388	−0.321380
12	1	0	0.400603	0.876891	−1.378317
13	1	0	−0.131744	2.019281	−0.108841
14	1	0	−1.218829	1.601397	−1.447878
15	1	0	0.306059	0.404880	1.763969
16	1	0	−0.280964	−1.323324	1.610730
17	1	0	1.115443	−0.678110	0.451970
18	1	0	2.519857	1.035129	−0.562209

Conformer 29 potential energy: 3.1 kcal/mol ground-state energy: 92.4 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.478532	−1.127319	−0.896626
2	6	0	−1.016026	−0.033551	0.022652
3	6	0	−0.034640	0.270447	1.132178
4	8	0	−2.248277	−0.450112	0.614352

5	6	0	−1.337784	1.224113	−0.768765
6	8	0	2.106675	0.746102	−0.090678
7	8	0	2.754715	−0.463733	0.099466
8	1	0	−2.107729	−1.270124	1.092004
9	1	0	0.392527	−0.762034	−1.450580
10	1	0	−1.248060	−1.416923	−1.617258
11	1	0	−0.183682	−2.014125	−0.323199
12	1	0	−0.427827	1.623855	−1.226357
13	1	0	−1.767287	1.983353	−0.109830
14	1	0	−2.062566	0.997276	−1.555045
15	1	0	−0.286389	1.128768	1.754886
16	1	0	0.334939	−0.592606	1.691797
17	1	0	1.116803	0.628024	0.514725
18	1	0	2.536256	−0.965661	−0.692899

Conformer 31 potential energy: 3.3 kcal/mol ground-state energy: 92.4 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.160530	1.160022	0.901674
2	6	0	−1.011530	−0.034348	−0.037253
3	6	0	−0.060249	0.296928	−1.163478
4	8	0	−2.255226	−0.306792	−0.686571
5	6	0	−0.532106	−1.266729	0.723632
6	8	0	2.076325	0.728353	0.096076
7	8	0	2.674178	−0.523310	0.087287
8	1	0	−2.901227	−0.553931	−0.021206
9	1	0	−0.201831	1.403967	1.369703
10	1	0	−1.879653	0.930234	1.695643
11	1	0	−1.521916	2.032222	0.349709
12	1	0	0.447482	−1.088410	1.176749
13	1	0	−0.454806	−2.121818	0.046303
14	1	0	−1.240402	−1.517599	1.521367
15	1	0	0.237052	−0.544739	−1.790052
16	1	0	−0.287740	1.210045	−1.713382
17	1	0	1.107500	0.587123	−0.532908
18	1	0	3.319816	−0.458343	−0.623713

Conformer 33 potential energy: 3.5 kcal/mol ground-state energy: 92.8 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.400240	−1.223696	−0.675143
2	6	0	1.003715	0.010717	−0.007099
3	6	0	0.017723	0.665927	0.922719
4	8	0	1.330579	0.994088	−0.980232
5	6	0	2.262643	−0.368543	0.786101
6	8	0	−2.180217	0.660307	−0.293917
7	8	0	−2.650366	−0.565437	0.157640
8	1	0	1.854068	0.587292	−1.672513
9	1	0	0.054825	−1.943381	0.073010
10	1	0	1.152356	−1.717376	−1.301369
11	1	0	−0.452526	−0.938323	−1.295613
12	1	0	2.033662	−1.106899	1.559982
13	1	0	2.696956	0.518075	1.255096
14	1	0	3.006818	−0.803611	0.109074
15	1	0	−0.313033	0.044388	1.755789
16	1	0	0.256228	1.695297	1.189409
17	1	0	−1.140502	0.769849	0.233332
18	1	0	−3.254747	−0.323403	0.866407

Conformer 35 potential energy: 3.6 kcal/mol ground-state energy: 92.7 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.786253	−1.423182	0.512252
2	6	0	−0.980115	0.007647	0.020049
3	6	0	−0.151277	0.977055	0.832383
4	8	0	−2.329023	0.423206	0.248172
5	6	0	−0.641380	0.121875	−1.464228
6	8	0	2.226329	0.730212	0.016929
7	8	0	2.422350	−0.633485	−0.146471
8	1	0	−2.910734	−0.108145	−0.299894
9	1	0	0.254502	−1.733745	0.383024
10	1	0	−1.420509	−2.109752	−0.059385
11	1	0	−1.060034	−1.498930	1.568433
12	1	0	0.390940	−0.186558	−1.653071
13	1	0	−0.771256	1.152971	−1.804691
14	1	0	−1.304816	−0.524113	−2.050689
15	1	0	−0.314116	2.025824	0.582431

16	1	0	−0.100035	0.780886	1.903417
17	1	0	1.140394	0.830533	0.424684
18	1	0	2.892564	−0.888803	0.653959

Conformer 37 potential energy: 3.8 kcal/mol ground-state energy: 93.1 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.226770	0.369678	−0.833593
2	6	0	−1.004215	−0.015123	0.010407
3	6	0	−0.009277	−0.734446	−0.859651
4	8	0	−1.386738	−0.940251	1.018411
5	6	0	−0.382120	1.229392	0.646213
6	8	0	2.214139	−0.660419	0.301949
7	8	0	2.707458	0.473967	−0.324877
8	1	0	−2.011903	−0.519377	1.611054
9	1	0	−1.952995	1.071691	−1.626368
10	1	0	−2.980389	0.850100	−0.198361
11	1	0	−2.669978	−0.521436	−1.285087
12	1	0	0.027867	1.895396	−0.120289
13	1	0	0.414721	0.927376	1.332570
14	1	0	−1.136052	1.788166	1.211738
15	1	0	−0.253455	−1.775812	−1.066126
16	1	0	0.346993	−0.169704	−1.722153
17	1	0	1.161425	−0.808880	−0.181406
18	1	0	2.509185	1.179100	0.300306

Conformer 39 potential energy: 3.9 kcal/mol ground-state energy: 93.1 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.381119	1.249349	−0.627998
2	6	0	−1.005912	−0.001566	−0.021259
3	6	0	−0.016954	−0.728451	0.859629
4	8	0	−1.386658	−0.810675	−1.124291
5	6	0	−2.243120	0.365259	0.809290
6	8	0	2.215112	−0.674321	−0.286507

7	8	0	2.709955	0.466581	0.325801
8	1	0	-1.827143	-1.600056	-0.804427
9	1	0	0.031620	1.891608	0.156165
10	1	0	-1.134041	1.810947	-1.186935
11	1	0	0.414135	0.956163	-1.320007
12	1	0	-1.982532	1.045835	1.624733
13	1	0	-2.697416	-0.530877	1.246061
14	1	0	-2.980176	0.851068	0.163002
15	1	0	0.336330	-0.171885	1.729708
16	1	0	-0.255732	-1.771391	1.075502
17	1	0	1.160349	-0.806115	0.185382
18	1	0	2.509970	1.164474	-0.307172

Conformer 41 potential energy: 4.1 kcal/mol ground-state energy: 93.1 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.308705	1.175315	0.834801
2	6	0	-1.012349	-0.037704	-0.042699
3	6	0	-0.031639	0.327787	-1.130754
4	8	0	-2.190500	-0.448743	-0.736264
5	6	0	-0.476790	-1.192684	0.802396
6	8	0	2.084044	0.724458	0.162472
7	8	0	2.773854	-0.442376	-0.126445
8	1	0	-2.878282	-0.639248	-0.094527
9	1	0	-0.393898	1.531055	1.319749
10	1	0	-2.030009	0.915574	1.617857
11	1	0	-1.727731	1.984676	0.230795
12	1	0	0.397117	-0.870875	1.378453
13	1	0	-0.206249	-2.039992	0.165731
14	1	0	-1.239037	-1.525865	1.515224
15	1	0	0.322909	-0.501110	-1.744384
16	1	0	-0.266133	1.233776	-1.688681
17	1	0	1.121336	0.640954	-0.478434
18	1	0	2.537687	-1.031934	0.597653

Conformer 43 potential energy: 4.1 kcal/mol ground-state energy: 93.3 kcal/mol

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	−0.408341	1.247537	−0.661251
2	6	0	−1.008251	0.003405	−0.019463
3	6	0	−0.019859	−0.653443	0.916946
4	8	0	−1.334490	−0.871515	−1.089770
5	6	0	−2.277726	0.359904	0.766239
6	8	0	2.186627	−0.672021	−0.284478
7	8	0	2.668134	0.551649	0.158445
8	1	0	−1.783018	−1.645333	−0.744110
9	1	0	−0.065156	1.947753	0.105596
10	1	0	−1.159820	1.738909	−1.284786
11	1	0	0.445735	0.971880	−1.284040
12	1	0	−2.060270	1.079623	1.560395
13	1	0	−2.717135	−0.532949	1.225289
14	1	0	−3.010890	0.798394	0.082723
15	1	0	0.313936	−0.034501	1.751938
16	1	0	−0.249296	−1.682742	1.199805
17	1	0	1.142230	−0.759608	0.226647
18	1	0	3.266586	0.309266	0.872144

Conformer 45 potential energy: 4.7 kcal/mol ground-state energy: 93.7 kcal/mol

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	1.015851	1.465183	−0.249927
2	6	0	1.076896	−0.038207	0.021397
3	6	0	−0.055072	−0.751682	−0.668760
4	8	0	0.911121	−0.297105	1.407783
5	6	0	2.414529	−0.618515	−0.457652
6	8	0	−2.133871	0.572247	−0.134178
7	8	0	−3.080946	−0.378955	0.208813
8	1	0	1.538527	0.231307	1.903670
9	1	0	1.077686	1.671173	−1.322777
10	1	0	1.855111	1.972897	0.238987
11	1	0	0.079960	1.878352	0.136388
12	1	0	2.554361	−0.455907	−1.530298
13	1	0	2.456943	−1.690880	−0.250882
14	1	0	3.240432	−0.129690	0.072071
15	1	0	−0.034282	−0.708767	−1.757368
16	1	0	−0.301811	−1.730576	−0.257183
17	1	0	−1.171988	−0.047000	−0.356618

18	1	0	−3.578599	−0.501082	−0.605682

TS of R2

Conformer 1 potential energy: 0 kcal/mol ground-state energy: 89.2 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.236565	−0.493620	−0.679379
2	6	0	−0.938564	−0.021920	0.009496
3	8	0	−0.042279	0.117508	−1.049607
4	6	0	−0.452215	−1.080622	0.998166
5	6	0	−1.165308	1.322947	0.698831
6	1	0	1.081318	0.478403	−0.650771
7	1	0	−3.008012	−0.619731	0.085994
8	1	0	−2.072416	−1.447568	−1.185258
9	1	0	−2.570753	0.247539	−1.408696
10	1	0	−1.207922	−1.255924	1.769751
11	1	0	0.471332	−0.749567	1.481866
12	1	0	−0.251497	−2.021084	0.477709
13	1	0	−1.910366	1.227114	1.494196
14	1	0	−0.227647	1.673133	1.141928
15	1	0	−1.512109	2.066035	−0.024214
16	8	0	2.013988	0.714652	−0.111252
17	8	0	2.633992	−0.496290	0.084598
18	1	0	3.118375	−0.646011	−0.735093

Conformer 3 potential energy: 0.6 kcal/mol ground-state energy: 89.9 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.212690	−0.563590	−0.669823
2	6	0	−0.938605	−0.018277	0.006255
3	8	0	−0.038489	0.116005	−1.047874
4	6	0	−0.421825	−1.027317	1.034031
5	6	0	−1.217260	1.336210	0.655252
6	1	0	1.098984	0.497297	−0.681618

7	1	0	−2.992157	−0.676918	0.089374
8	1	0	−2.012500	−1.533918	−1.129647
9	1	0	−2.558802	0.131264	−1.438041
10	1	0	−1.199426	−1.267219	1.765130
11	1	0	0.429214	−0.600831	1.576431
12	1	0	−0.108641	−1.948411	0.534056
13	1	0	−1.951226	1.237185	1.460782
14	1	0	−0.291638	1.741461	1.076889
15	1	0	−1.600189	2.040317	−0.088020
16	8	0	1.992080	0.704927	−0.078720
17	8	0	2.715680	−0.461437	−0.130401
18	1	0	2.574497	−0.858336	0.736337

Conformer 5 potential energy: 1.8 kcal/mol ground-state energy: 90.9 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.363468	−0.375862	−0.355946
2	6	0	0.919215	0.024867	−0.000340
3	8	0	0.132938	−0.724925	−0.873248
4	6	0	0.715322	1.523501	−0.219046
5	6	0	0.624452	−0.379642	1.448226
6	1	0	−1.092843	−0.694147	−0.664491
7	1	0	3.053938	0.188799	0.277924
8	1	0	2.571942	−0.143557	−1.402860
9	1	0	2.512570	−1.445261	−0.191399
10	1	0	1.348883	2.103841	0.458868
11	1	0	−0.328344	1.797312	−0.044723
12	1	0	0.970764	1.788353	−1.248803
13	1	0	1.307720	0.134068	2.130648
14	1	0	−0.401481	−0.110571	1.717379
15	1	0	0.740224	−1.459567	1.568403
16	8	0	−2.110498	−0.753242	−0.232797
17	8	0	−2.502080	0.541469	0.005615
18	1	0	−2.581004	0.577127	0.965134

***tert*–butanol** potential energy: 0 kcal/mol ground-state energy: 82.7 kcal/mol

Center	Atomic	Atomic	Coordinates (Angstroms)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.006082	0.000000	0.019773
2	8	0	0.050068	-0.000013	1.444478
3	6	0	-1.487648	-0.000041	-0.326208
4	6	0	0.673507	1.255264	-0.522436
5	6	0	0.673583	-1.255213	-0.522459
6	1	0	0.968257	0.000002	1.720551
7	1	0	-1.629191	-0.000022	-1.410776
8	1	0	-1.971471	0.886836	0.092130
9	1	0	-1.971415	-0.886968	0.092090
10	1	0	0.608392	1.295969	-1.614155
11	1	0	1.734767	1.268754	-0.248056
12	1	0	0.198252	2.148970	-0.108667
13	1	0	0.608479	-1.295901	-1.614179
14	1	0	1.734842	-1.268645	-0.248072
15	1	0	0.198380	-2.148955	-0.108707

HO_2 potential energy: 0 kcal/mol ground-state energy: 9.0 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.875517	-0.869527	0.000000
2	8	0	0.054720	-0.597182	0.000000
3	8	0	0.054720	0.705873	0.000000

H_2O_2 potential energy: 0 kcal/mol ground-state energy: 16.8 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-1.019829	0.629889	0.460298
2	8	0	-0.700574	-0.114617	-0.057537
3	8	0	0.700574	0.114617	-0.057537
4	1	0	1.019830	-0.629889	0.460299

$CH_2{\cdot}(CH_3)_2COH$

Conformer 1 potential energy: 0 kcal/mol ground-state energy: 73.8 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.117384	−0.947386	−0.352144
2	6	0	0.003385	0.042063	−0.006145
3	6	0	0.109691	1.275017	−0.841962
4	8	0	0.219483	0.369525	1.368611
5	6	0	−1.364935	−0.617509	−0.176399
6	1	0	0.072387	−0.417685	1.896305
7	1	0	1.025988	−1.284120	−1.387967
8	1	0	1.053485	−1.814681	0.312399
9	1	0	2.093651	−0.475525	−0.216672
10	1	0	−1.525743	−0.913912	−1.217578
11	1	0	−2.165191	0.074265	0.107463
12	1	0	−1.430482	−1.505446	0.457615
13	1	0	0.924431	1.964948	−0.658253
14	1	0	−0.527062	1.425706	−1.704404

Conformer 3 potential energy: 1.0 kcal/mol ground-state energy: 74.5 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.097005	−0.989293	−0.397510
2	6	0	0.018091	0.029077	−0.000041
3	6	0	0.126728	1.257806	−0.835151
4	8	0	0.223179	0.441439	1.347322
5	6	0	−1.372000	−0.602486	−0.145853
6	1	0	0.185556	−0.329285	1.916055
7	1	0	0.985576	−1.287139	−1.444082
8	1	0	1.013020	−1.890174	0.222833
9	1	0	2.090619	−0.556937	−0.257820
10	1	0	−1.566852	−0.879224	−1.186239
11	1	0	−2.139982	0.102362	0.181184
12	1	0	−1.441906	−1.510037	0.465531
13	1	0	0.468197	2.181069	−0.389671
14	1	0	−0.080760	1.208080	−1.895689

$(CH_3)_3CO^{\cdot}$ potential energy: 0 kcal/mol ground-state energy: 74.5 kcal/mol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.266429	−0.787763	−0.311550
2	6	0	0.000001	−0.023374	0.080101
3	8	0	−0.000013	0.264646	1.427833
4	6	0	−0.000061	1.374332	−0.580253
5	6	0	1.266500	−0.787651	−0.311548
6	1	0	−1.290482	−0.964540	−1.391167
7	1	0	−2.154049	−0.218487	−0.024336
8	1	0	−1.295653	−1.756416	0.195328
9	1	0	−0.000041	1.238642	−1.665533
10	1	0	0.890753	1.934740	−0.288637
11	1	0	−0.890937	1.934651	−0.288657
12	1	0	1.290563	−0.964442	−1.391163
13	1	0	2.154069	−0.218290	−0.024347
14	1	0	1.295817	−1.756293	0.195346

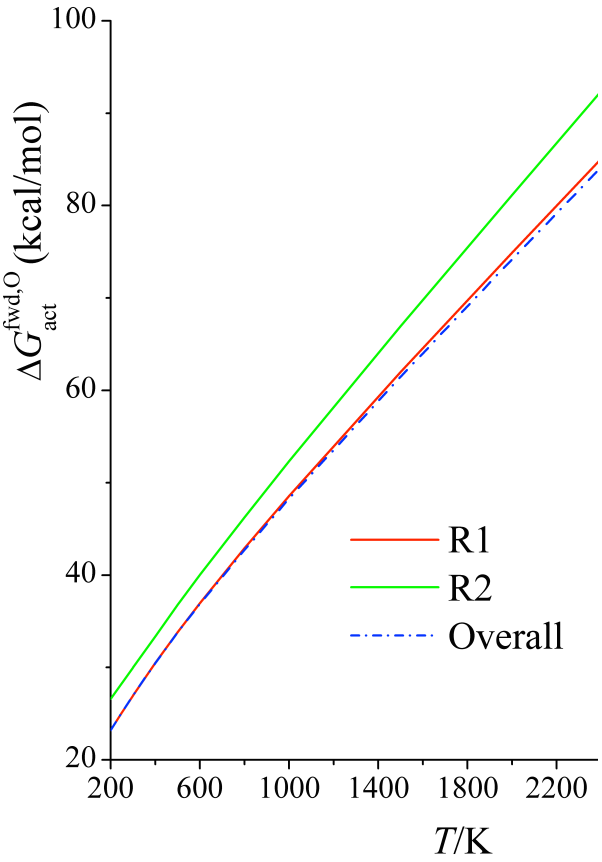
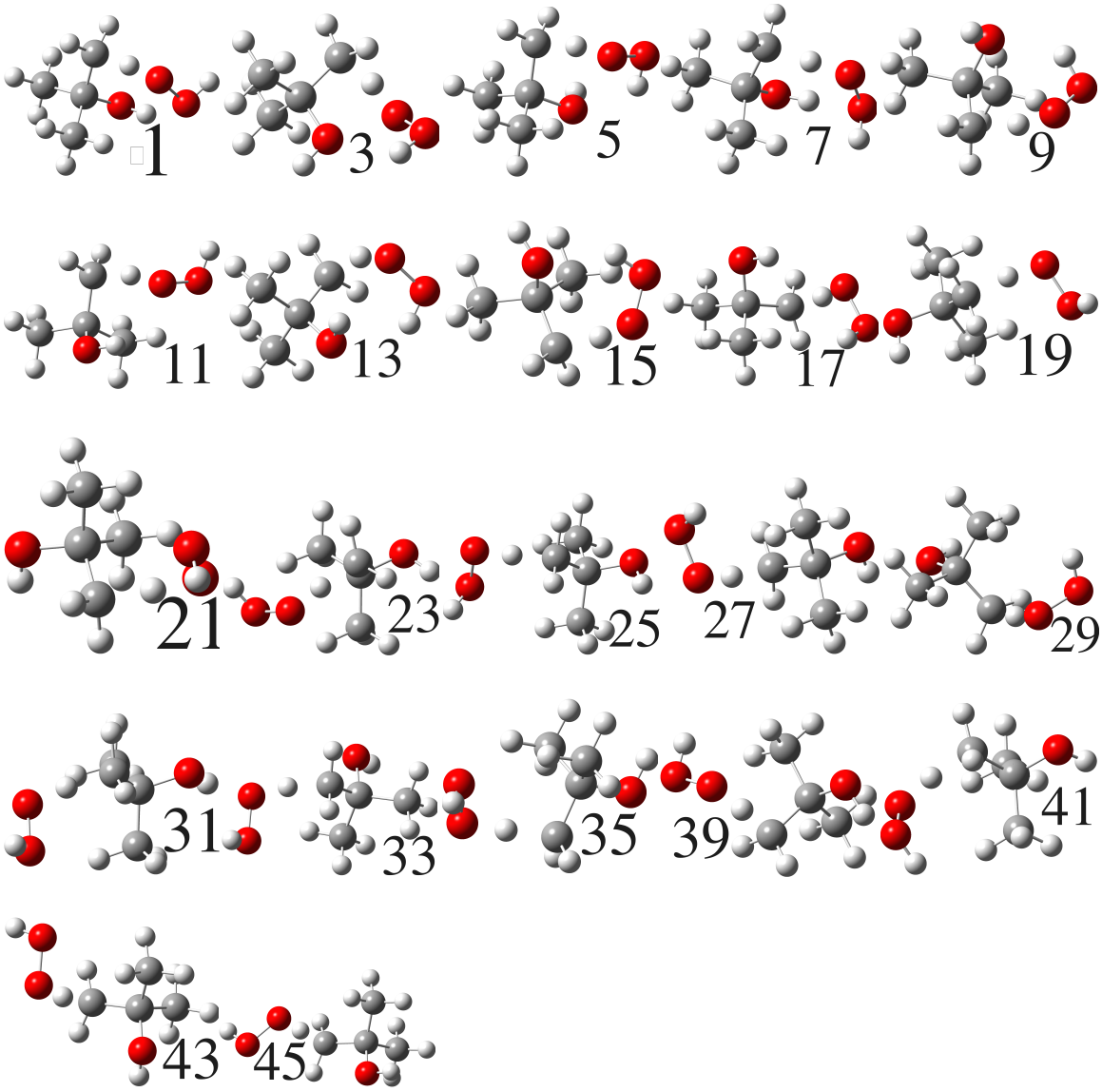


Figure S1. Phenomenological Gibbs free energy of activation (in kcal/mol) for forward reactions R1, R2 and the overall reaction at various temperatures.

Figure S2. Geometries of conformers of transition state structures for reaction R1 and R2. When conformations occur in enantiomeric pairs, only one enantiomer is shown and so only structures with odd structure numbers occur in the figure in those cases.

TS of Reaction R1:



TS of Reaction R2: