SUPPORTING INFORMATION

Multi-path variational transition state theory for chiral molecules: The site-dependent kinetics for abstraction of hydrogen from 2-butanol by hydroperoxyl radical, analysis of hydrogen bonding in the transition state, and dramatic temperature dependence of the activation energy

Junwei Lucas Bao, Rubén Meana Pañeda, and Donald G. Truhlar
Department of Chemistry, Chemical Yheory Center, and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431

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T/K	TS1			TS2			TS3			TS4			TS5		
	$Q^{\text{SS-QH}}$	$Q^{\text{MS-T}}$	$F_X^{\text{MS-T}}$	$Q^{\text{SS-QH}}$	$Q^{\text{MS-T}}$	$F_X^{\text{MS-T}}$	$Q^{\text{SS-QH}}$	$Q^{\text{MS-T}}$	$F_X^{\text{MS-T}}$	$Q^{\text{SS-QH}}$	$Q^{\text{MS-T}}$	$F_X^{\text{MS-T}}$	$Q^{\text{SS-QH}}$	$Q^{\text{MS-T}}$	$F_X^{\text{MS-T}}$
200	3.04E-92	5.38E-92	1.7675	5.56E-93	9.75E-93	1.756	1.31E-92	3.94E-92	3.0175	2.59E-93	2.20E-93	0.85079	1.04E-91	1.85E-91	1.7719
298.15	1.82E-58	5.58E-58	3.0684	4.94E-59	1.59E-58	3.217	7.72E-59	4.47E-58	5.7817	1.79E-59	2.47E-59	1.3803	3.73E-58	1.29E-57	3.458
300	4.91E-58	1.52E-57	3.0955	1.34E-58	4.36E-58	3.249	2.09E-58	1.22E-57	5.8434	4.83E-59	6.75E-59	1.3971	1.00E-57	3.51E-57	3.4986
400	2.36E-40	1.11E-39	4.7255	7.98E-41	4.15E-40	5.196	1.01E-40	9.87E-40	9.7795	2.41E-41	7.15E-41	2.9669	3.63E-40	2.22E-39	6.123
500	2.64E-29	1.76E-28	6.6859	1.01E-29	7.55E-29	7.426	1.14E-29	1.68E-28	14.766	2.73E-30	1.76E-29	6.4415	3.38E-29	3.17E-28	9.3846
600	1.37E-21	1.21E-20	8.8821	5.70E-22	5.55E-21	9.759	5.93E-22	1.21E-20	20.431	1.42E-22	1.75E-21	12.38	1.54E-21	1.98E-20	12.921
800	3.21E-11	4.29E-10	13.36	1.46E-11	2.07E-10	14.148	1.40E-11	4.46E-10	31.94	3.30E-12	1.02E-10	30.893	3.01E-11	5.91E-10	19.638
900	1.82E-07	2.80E-06	15.376	8.52E-08	1.37E-06	16.009	7.93E-08	2.94E-06	37.069	1.86E-08	7.86E-07	42.148	1.60E-07	3.60E-06	22.459
1000	2.67E-04	4.58E-03	17.138	1.28E-04	2.25E-03	17.584	1.16E-04	4.83E-03	41.505	2.73E-05	1.46E-03	53.711	2.24E-04	5.55E-03	24.816
1200	3.61E+01	7.14E+02	19.796	1.77E+01	3.51E+02	19.849	1.57E+01	7.55E+02	48.063	3.65E+00	2.75E+02	75.416	2.80E+01	7.86E+02	28.124
1400	4.14E+05	8.84E+06	21.352	2.06E+05	4.34E+06	21.051	1.80E+05	9.31E+06	51.722	4.17E+04	3.87E+06	92.954	3.04E+05	9.06E+06	29.783
1500	2.33E+07	5.08E+08	21.776	1.17E+07	2.49E+08	21.321	1.01E+07	5.34E+08	52.633	2.34E+06	2.34E+08	99.821	1.68E+07	5.06E+08	30.113
1800	6.84E+11	1.50E+13	21.984	3.46E+11	7.35E+12	21.160	2.97E+11	1.57E+13	52.652	6.83E+10	7.73E+12	113.11	4.71E+11	1.40E+13	29.689
2000	2.14E+14	4.61E+15	21.499	1.09E+14	2.24E+15	20.498	9.31E+13	4.76E+15	51.12	2.14E+13	2.50E+15	116.84	1.45E+14	4.14E+15	28.621
2500	2.91E+19	5.59E+20	19.219	1.49E+19	2.68E+20	17.949	1.26E+19	5.66E+20	44.812	2.89E+18	3.31E+20	114.6	1.90E+19	4.70E+20	24.772
3000	3.49E+23	5.76E+24	16.479	1.80E+23	2.72E+24	15.106	1.52E+23	5.71E+24	37.68	3.46E+22	3.60E+24	104.04	2.23E+23	4.61E+24	20.644

Table S2. Multi-path CVT/SCT (averaged over four lowest-energy paths) and multi-structural CVT/SCT forward reaction constants (units: $cm^3 molecule^{-1} s^{-1}$) for reactions R1-R5 at various temperatures.

T/K	R1		R2		R3		R4		R5		Total	
	$k^{MP\text{-}CVT/SCT}$	$k^{MS\text{-}CVT/SCT}$	$k^{MP\text{-}CVT/SCT}$	$k^{MS\text{-}CVT/SCT}$	$k^{MP\text{-}CVT/SCT}$	$k^{MS\text{-}CVT/SCT}$	$k^{MP\text{-}CVT/SCT}$	$k^{MS\text{-}CVT/SCT}$	$k^{MP\text{-}CVT/SCT}$	$k^{MS\text{-}CVT/SCT}$	$k^{MP\text{-}CVT/SCT}$	$k^{MS\text{-}CVT/SCT}$
200	2.00E-33	1.61E-33	1.76E-25	1.37E-25	4.09E-30	3.86E-30	8.42E-32	5.63E-32	4.42E-36	2.04E-36	1.76E-25	1.37E-25
298.15	1.40E-27	1.26E-27	2.51E-22	2.29E-22	2.20E-25	2.15E-25	8.30E-27	6.26E-27	4.82E-29	2.90E-29	2.51E-22	2.29E-22
300	1.66E-27	1.50E-27	2.78E-22	2.54E-22	2.54E-25	2.48E-25	9.68E-27	7.31E-27	5.93E-29	3.59E-29	2.78E-22	2.54E-22
400	2.48E-24	2.33E-24	2.13E-20	2.01E-20	1.09E-22	1.07E-22	6.72E-24	5.53E-24	3.28E-25	2.30E-25	2.14E-20	2.02E-20
500	2.80E-22	2.69E-22	4.00E-19	3.81E-19	5.92E-21	5.75E-21	5.72E-22	4.96E-22	7.43E-23	5.69E-23	4.07E-19	3.88E-19
600	8.21E-21	8.02E-21	3.44E-18	2.57E-18	1.06E-19	1.02E-19	1.47E-20	1.32E-20	3.25E-21	2.64E-21	3.57E-18	2.70E-18
800	8.22E-19	8.11E-19	6.55E-17	4.71E-17	5.65E-18	5.27E-18	1.26E-18	1.16E-18	4.79E-19	4.16E-19	7.37E-17	5.48E-17
900	4.32E-18	4.27E-18	1.90E-16	1.37E-16	2.39E-17	2.20E-17	6.24E-18	5.79E-18	2.79E-18	2.47E-18	2.27E-16	1.72E-16
1000	1.72E-17	1.71E-17	4.68E-16	3.35E-16	7.99E-17	7.27E-17	2.36E-17	2.20E-17	1.19E-17	1.08E-17	6.01E-16	4.58E-16
1200	1.54E-16	1.53E-16	1.94E-15	1.41E-15	5.45E-16	4.79E-16	1.92E-16	1.78E-16	1.16E-16	1.08E-16	2.95E-15	2.33E-15
1400	8.11E-16	8.08E-16	5.85E-15	4.25E-15	2.35E-15	2.02E-15	9.29E-16	8.61E-16	6.47E-16	6.13E-16	1.06E-14	8.55E-15
1500	1.62E-15	1.62E-15	9.25E-15	6.75E-15	4.34E-15	3.68E-15	1.79E-15	1.65E-15	1.32E-15	1.26E-15	1.83E-14	1.50E-14
1800	8.81E-15	8.85E-15	2.92E-14	2.13E-14	1.93E-14	1.58E-14	8.84E-15	8.05E-15	7.41E-15	7.21E-15	7.36E-14	6.12E-14
2000	2.15E-14	2.16E-14	5.35E-14	3.94E-14	4.27E-14	3.38E-14	2.05E-14	1.83E-14	1.85E-14	1.80E-14	1.57E-13	1.31E-13
2500	1.18E-13	1.20E-13	1.77E-13	1.30E-13	1.93E-13	1.41E-13	9.97E-14	8.71E-14	1.04E-13	1.03E-13	6.92E-13	5.81E-13
3000	4.02E-13	4.12E-13	4.23E-13	3.11E-13	5.36E-13	1.58E-13	2.75E-13	9.56E-14	3.59E-13	3.60E-13	2.00E-12	1.34E-12

Table S3. Multi-path CVT/SCT (averaged over four lowest-energy paths) and multi-structural CVT/SCT reverse reaction constants (units: cm^3 $molecule^{-1}$ s^{-1}) for reactions R1-R5 at various temperatures.

T/K	R1		R2		R3		R4		R5		Total	
	$k^{MP\text{-}CVT/SCT}$	$k^{MS\text{-}CVT/SCT}$	$k^{MP\text{-}CVT/SCT}$	$k^{MS\text{-}CVT/SCT}$	$k^{MP\text{-}CVT/SCT}$	$k^{MS\text{-}CVT/SCT}$	$k^{MP\text{-}CVT/SCT}$	$k^{MS\text{-}CVT/SCT}$	$k^{MP\text{-}CVT/SCT}$	$k^{MS\text{-}CVT/SCT}$	$k^{MP\text{-}CVT/SCT}$	$k^{MS\text{-}CVT/SCT}$
200	2.11E-17	1.70E-17	3.38E-19	2.63E-19	9.44E-18	8.90E-18	2.65E-17	1.78E-17	1.93E-15	8.92E-16	1.99E-15	9.36E-16
298.15	3.65E-17	3.28E-17	1.26E-18	1.15E-18	1.77E-17	1.74E-17	2.34E-17	1.77E-17	3.12E-15	1.88E-15	3.20E-15	1.95E-15
300	3.69E-17	3.33E-17	1.30E-18	1.18E-18	1.80E-17	1.76E-17	2.36E-17	1.78E-17	3.15E-15	1.91E-15	3.23E-15	1.98E-15
400	7.20E-17	6.80E-17	4.58E-18	4.33E-18	3.88E-17	3.81E-17	4.09E-17	3.37E-17	5.79E-15	4.05E-15	5.95E-15	4.19E-15
500	1.43E-16	1.38E-16	1.33E-17	1.26E-17	8.35E-17	8.14E-17	9.00E-17	7.80E-17	1.03E-14	7.90E-15	1.06E-14	8.21E-15
600	2.75E-16	2.68E-16	3.25E-17	2.43E-17	1.71E-16	1.64E-16	1.95E-16	1.75E-16	1.75E-14	1.42E-14	1.82E-14	1.48E-14
800	8.74E-16	8.62E-16	1.30E-16	9.40E-17	5.91E-16	5.51E-16	7.27E-16	6.72E-16	4.30E-14	3.74E-14	4.53E-14	3.96E-14
900	1.44E-15	1.43E-15	2.27E-16	1.64E-16	1.00E-15	9.21E-16	1.25E-15	1.16E-15	6.33E-14	5.63E-14	6.72E-14	6.00E-14
1000	2.27E-15	2.25E-15	3.73E-16	2.68E-16	1.62E-15	1.47E-15	2.02E-15	1.89E-15	9.00E-14	8.15E-14	9.63E-14	8.74E-14
1200	5.01E-15	4.99E-15	8.60E-16	6.20E-16	3.71E-15	3.27E-15	4.58E-15	4.26E-15	1.67E-13	1.56E-13	1.81E-13	1.69E-13
1400	9.79E-15	9.79E-15	1.72E-15	1.25E-15	7.43E-15	6.39E-15	8.94E-15	8.29E-15	2.84E-13	2.69E-13	3.12E-13	2.95E-13
1500	1.32E-14	1.32E-14	2.33E-15	1.70E-15	1.01E-14	8.59E-15	1.20E-14	1.11E-14	3.59E-13	3.43E-13	3.97E-13	3.78E-13
1800	2.87E-14	2.88E-14	5.15E-15	3.78E-15	2.26E-14	1.84E-14	2.55E-14	2.32E-14	6.66E-13	6.48E-13	7.48E-13	7.22E-13
2000	4.46E-14	4.48E-14	8.05E-15	5.90E-15	3.55E-14	2.81E-14	3.88E-14	3.49E-14	9.52E-13	9.30E-13	1.08E-12	1.04E-12
2500	1.10E-13	1.11E-13	2.01E-14	1.47E-14	8.86E-14	6.49E-14	9.05E-14	7.91E-14	1.97E-12	1.95E-12	2.28E-12	2.22E-12
3000	2.23E-13	2.28E-13	4.08E-14	2.98E-14	1.69E-13	4.97E-14	1.55E-13	5.38E-14	3.48E-12	3.49E-12	4.07E-12	3.85E-12

Table S4. Averaged generalized transmission coefficients[a] of reactions R1-R5 at various temperatures.[a,b]

T/K	R1				R2				R3				R4				R5			
	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_3$	$\langle\gamma\rangle_4$	URE (%)	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_3$	$\langle\gamma\rangle_4$	URE (%)	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_3$	$\langle\gamma\rangle_4$	URE (%)	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_3$	$\langle\gamma\rangle_4$	URE (%)	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_3$	$\langle\gamma\rangle_4$	URE (%)
200	196.5	231.8	243.5	4.8	20.84	26.94	26.88	0.2	207.0	214.7	218.6	1.8	45.43	59.42	67.68	12.2	1.42	1.78	1.95	8.4
298.15	17.58	18.95	19.54	3.0	3.83	4.19	4.15	0.9	17.49	17.67	17.80	0.8	8.16	9.78	10.80	9.4	1.18	1.36	1.44	5.8
300	17.04	18.37	18.95	3.0	3.74	4.12	4.08	1.0	17.09	17.20	17.32	0.7	7.99	9.56	10.55	9.3	1.18	1.35	1.44	5.8
400	5.79	6.00	6.13	2.2	2.02	2.12	2.11	0.8	5.62	5.63	5.66	0.4	3.62	4.08	4.37	6.6	1.10	1.20	1.25	4.2
500	3.28	3.34	3.39	1.6	1.50	1.56	1.55	0.9	3.09	3.12	3.14	0.5	2.35	2.55	2.68	4.8	1.06	1.12	1.16	3.0
600	2.33	2.35	2.38	1.5	1.27	1.32	1.31	0.9	2.19	2.21	2.23	0.6	1.80	1.91	1.98	3.6	1.04	1.08	1.10	2.4
800	1.63	1.63	1.65	1.2	0.90	1.05	1.03	2.2	1.50	1.53	1.54	0.8	1.35	1.38	1.42	2.2	1.02	1.03	1.05	1.7
900	1.46	1.46	1.48	1.2	0.81	0.97	0.94	2.9	1.33	1.38	1.39	0.9	1.24	1.26	1.28	1.7	1.01	1.02	1.03	1.5
1000	1.36	1.35	1.37	1.2	0.73	0.90	0.87	3.3	1.23	1.27	1.29	1.1	1.16	1.17	1.18	1.5	1.01	1.01	1.02	1.5
1200	1.23	1.22	1.23	1.3	0.63	0.79	0.77	3.4	1.09	1.14	1.16	1.4	1.05	1.05	1.06	1.2	1.01	0.99	1.00	1.4
1400	1.16	1.14	1.15	1.3	0.57	0.72	0.69	3.5	1.01	1.06	1.08	1.7	0.98	0.97	0.98	1.0	1.00	0.98	0.99	1.3
1500	1.13	1.11	1.13	1.4	0.54	0.69	0.66	3.6	0.98	1.04	1.06	1.8	0.96	0.95	0.95	0.9	1.00	0.98	0.99	1.3
1800	1.08	1.05	1.07	1.6	0.48	0.62	0.60	3.6	0.91	0.98	1.00	2.2	0.90	0.88	0.89	0.8	1.00	0.97	0.98	1.1
2000	1.06	1.03	1.05	1.7	0.45	0.59	0.57	3.6	0.87	0.95	0.97	2.5	0.87	0.85	0.85	0.9	1.00	0.97	0.98	1.3
2400	1.03	0.98	1.01	2.4	0.42	0.54	0.53	3.3	0.79	0.89	0.92	3.3	0.80	0.79	0.78	0.6	1.00	0.96	0.97	1.4
2500	1.03	0.98	1.00	2.2	0.41	0.54	0.52	3.7	0.81	0.89	0.92	3.0	0.81	0.78	0.79	0.7	1.00	0.96	0.97	1.4
3000	1.01	0.95	0.98	2.9	0.38	0.50	0.48	3.7	0.63	0.78	0.83	5.6	0.68	0.68	0.66	3.4	1.00	0.95	0.97	1.5

[a] Generalized transmission coefficients averaged over the p lowest-energy path(s) are denoted as $\langle\gamma\rangle_p$.

[b] URE is unsigned relative error $= \left|\langle\gamma\rangle_4 - \langle\gamma\rangle_3\right| / \langle\gamma\rangle_4$

Table S5. M08-HX/MG3S optimized Cartesian coordinates (in Å) of the lowest-energy structures of the reactants, products and the transition state structures

S-2-butanol

C	-1.782357	-0.668644	-0.001191
H	-1.905577	-0.735454	-1.086729
H	-1.798639	-1.679997	0.415628
H	-2.639175	-0.122900	0.408297
C	-0.474061	0.033822	0.327623
H	-0.349723	0.084476	1.423478
C	0.725192	-0.693972	-0.259082
H	0.706040	-1.732393	0.092121
H	0.600377	-0.721191	-1.349211
C	2.047180	-0.030006	0.105611
H	2.186481	-0.011249	1.191808
H	2.895711	-0.562431	-0.331497
H	2.066894	1.002178	-0.251843
O	-0.455936	1.349245	-0.208774
H	-1.210628	1.837803	0.120363

HO_2

O	0.054720	-0.597182	0.000000
H	-0.875517	-0.869525	0.000000
O	0.054720	0.705873	0.000000

H_2O_2

O	-0.700566	-0.114624	-0.057532
H	-1.019842	0.629930	0.460220
O	0.700567	0.114613	-0.057540
H	1.019833	-0.629841	0.460363

P1

C	-1.801222	-0.697546	0.003224	H	-2.172547	-1.502757	0.623092
C	-0.528888	-0.003459	0.330001	H	-2.272130	-0.508455	-0.954214
H	-0.387073	0.010262	1.425506				
C	0.689396	-0.698235	-0.286940				
H	0.692154	-1.744640	0.037442				
H	0.557988	-0.696966	-1.375489				
C	1.994078	-0.010185	0.097517				
H	2.130574	-0.015425	1.184150				
H	2.854105	-0.513842	-0.351189				
H	1.990620	1.030129	-0.235242				
O	-0.525235	1.327604	-0.169632				
H	-1.311995	1.777416	0.140189				

P2

C	1.812273	-0.650720	-0.108042
H	2.188232	-0.729353	0.926870
H	1.753147	-1.662427	-0.516103
H	2.564306	-0.100683	-0.686784
C	0.483257	0.017366	-0.162300
C	-0.747013	-0.695225	0.280004
H	-0.699001	-1.726651	-0.085521

H	-0.757377	-0.760143	1.383871
C	-2.032718	-0.018165	-0.192271
H	-2.070748	0.018166	-1.284778
H	-2.914200	-0.556144	0.165469
H	-2.083182	1.008475	0.177782
O	0.454419	1.353291	0.138556
H	1.288676	1.762897	-0.093595

P3

C	-1.773418	-0.679621	-0.042165
H	-1.867590	-0.734968	-1.132767
H	-1.786963	-1.701089	0.349630
H	-2.635511	-0.138364	0.352996
C	-0.480927	0.028845	0.337978
H	-0.415523	0.088382	1.437362
C	0.724723	-0.668234	-0.197219
C	2.079662	-0.107861	0.034724
H	2.491899	-0.440149	1.001071
H	2.791256	-0.419573	-0.734767
H	2.046665	0.985544	0.062005
O	-0.506577	1.397220	-0.066885
H	-0.486211	1.423177	-1.026098
H	0.614351	-1.679493	-0.574271

P4

C	1.759519	-0.606837	-0.002693	H	-0.386559	1.758836	0.138545

H	1.879702	-0.676481	1.082898	H	-2.221691	0.255676	-1.127075
H	1.805332	-1.613442	-0.427147	H	-2.897719	-0.104255	0.561803
H	2.589924	-0.019574	-0.401159				
C	0.437969	0.056296	-0.331170				
H	0.316147	0.106652	-1.427649				
C	-0.752890	-0.713791	0.246090				
H	-0.705196	-1.749504	-0.132245				
H	-0.635450	-0.774897	1.335089				
C	-2.052691	-0.090419	-0.112711				
O	0.488008	1.368188	0.199981				
P5							
C	-1.835106	-0.579070	0.025515				
H	-1.990911	-0.724941	-1.047602				
H	-1.856002	-1.559405	0.508874				
H	-2.654742	0.028403	0.414244				
C	-0.495235	0.114378	0.263432				
H	-0.358068	0.255692	1.360038				
C	0.704852	-0.685697	-0.257261				
H	0.640063	-1.705964	0.138003				
H	0.606242	-0.765098	-1.347088				
C	2.033136	-0.042194	0.113807				
H	2.167519	-0.021886	1.200517				
H	2.876731	-0.586696	-0.317037				
H	2.070338	0.989046	-0.246294				
O	-0.493382	1.405794	-0.192076				

TS1

C	-0.398703	1.387700	0.080526	H	-0.587870	-1.120717	0.875018
C	0.480812	0.180509	-0.092518	H	-0.379137	1.821209	1.081389
H	0.258327	-0.300836	-1.062358	H	-0.376643	2.120106	-0.726643
C	1.959424	0.577042	-0.091487	O	-2.333812	-0.979293	-0.311588
H	2.119264	1.348591	-0.852993	H	-2.438791	-1.049345	-1.265714
H	2.181615	1.030074	0.882118	O	-2.687793	0.334322	-0.032845
C	2.865388	-0.622988	-0.339698	H	-1.653854	0.904947	0.030248
H	2.661983	-1.068475	-1.319161				
H	3.919164	-0.334229	-0.314391				
H	2.697430	-1.388934	0.420485				
O	0.291228	-0.742024	0.958316				

TS2

C	1.708284	1.436957	-0.347782	H	-0.020086	-2.202057	1.079191
H	2.650407	1.296029	0.196893	O	0.363026	0.487711	1.349948
H	1.921730	1.405684	-1.418531	H	-0.319210	-0.160893	1.550522
H	1.311512	2.421790	-0.092017	O	-1.580642	0.607008	-0.949014
C	0.735174	0.354938	0.029048	H	-0.368612	0.564825	-0.627015
C	1.118516	-1.054152	-0.385589	O	-2.210839	0.280843	0.241998
H	1.278057	-1.054293	-1.469283	H	-2.403376	1.138167	0.636016
H	2.087489	-1.291301	0.079129				
C	0.076862	-2.102813	-0.007609				
H	-0.903789	-1.845484	-0.418732				
H	0.360499	-3.086544	-0.388040				

TS3 (2*S*, 3*R*)

C	-2.275261	-0.762699	-0.420765	O	-0.427294	-1.032482	1.025644
H	-2.773362	-0.166682	0.349327	H	0.528335	-1.123268	1.076421
H	-2.615054	-0.426709	-1.404111	H	-0.413278	1.105765	-1.588528
H	-2.560992	-1.807959	-0.282689	O	2.163440	0.581165	-0.167961
C	-0.764019	-0.618460	-0.281478	H	0.984664	0.748737	-0.382695
H	-0.275384	-1.274049	-1.021186	O	2.287976	-0.793023	-0.013180
C	-0.327264	0.811031	-0.538750	H	2.574328	-1.099215	-0.879385
C	-0.784011	1.846693	0.451371				
H	-0.664172	1.477712	1.472877				
H	-0.228304	2.781298	0.343317				
H	-1.846434	2.079689	0.298364				

TS3 (2*S*, 3*S*)

C	1.971665	-0.855892	-0.564108	H	-1.371783	2.397752	-0.694815
H	1.253200	-1.615921	-0.885088	H	-1.195731	1.543705	0.848386
H	2.479609	-0.451982	-1.444529	O	0.577368	-0.278732	1.338360
H	2.726595	-1.330608	0.070752	H	1.221885	-0.699449	1.908448
C	1.242498	0.246308	0.187860	O	-2.023912	-0.841909	0.361150
H	1.966628	1.013641	0.520567	H	-1.349650	-1.008635	1.034569
C	0.200383	0.925392	-0.662943	O	-1.330250	-1.055191	-0.817634
H	0.569255	1.177349	-1.659116				
H	-0.655280	-0.104488	-0.916899				
C	-0.649299	1.967802	0.001503				
H	-0.021866	2.783632	0.388840				

TS4

C	-2.503742	-0.477287	0.351305	H	0.249406	-0.789536	-1.270152
H	-2.196361	-0.977000	1.275599	H	1.217351	2.430942	0.373153
H	-3.193363	0.331194	0.607306	H	0.491838	2.003374	-1.241157
H	-3.027619	-1.203981	-0.273067	O	1.882075	-0.931178	0.804247
C	-1.286054	0.061574	-0.371882	H	1.059587	-1.394867	0.581287
H	-1.602900	0.561952	-1.301822	O	2.193689	-0.280718	-0.377959
C	-0.519469	1.066761	0.489159	H	1.589682	0.706876	-0.325197
H	-1.221543	1.853837	0.806859				
H	-0.187472	0.567417	1.410380				
C	0.650560	1.701961	-0.203732				
O	-0.479059	-1.064137	-0.705324				

TS5

C	1.987982	-1.358319	0.307646	H	0.439538	3.096879	0.029950
H	2.714611	-1.248776	-0.502564	H	-0.395483	1.899668	-0.968326
H	2.494361	-1.164558	1.256634	O	0.150769	-0.680522	-1.041556
H	1.614891	-2.384355	0.301886	O	-2.060139	-0.347968	0.850305
C	0.842125	-0.365914	0.104554	H	-2.334345	-1.241732	1.088209
H	0.119440	-0.509994	0.948577	O	-2.113879	-0.345169	-0.518509
C	1.288114	1.096812	0.135314	H	-1.062886	-0.445119	-0.870303
H	1.818728	1.278149	1.077499				
H	2.013984	1.247451	-0.673863				
C	0.112894	2.055115	-0.012813				
H	-0.623539	1.895491	0.782180				

Table S6. Forward and reverse classical barrier heights and classical energies of reaction (kcal/mol) for R1–R5[a]

Electronic model chemistry	Forward barrier height $V_f^{\ddagger}$					Reverse barrier height $V_r^{\ddagger}$					Energy of reaction ΔE (kcal/mol)					MUE	MUE (w/o
//M08-HX/MG3S	R1	R2	R3	R4	R5	R1	R2	R3	R4	R5	R1	R2	R3	R4	R5		R5)
M08-HX/aug-cc-pVTZ	20.89	12.09	17.66	17.61	22.07	4.46	4.64	4.37	2.83	2.23	16.44	7.45	13.28	14.78	19.84	0.22	0.21
M08-SO/aug-cc-pVTZ	21.92	13.10	18.56	18.39	21.94	5.06	5.19	5.35	3.00	1.41	16.86	7.90	13.20	15.39	20.52	0.66	0.70
M06-2X/aug-cc-pVTZ	19.02	10.61	15.87	15.71	19.83	3.11	3.36	3.20	1.40	0.43	15.90	7.25	12.67	14.31	19.40	1.14	1.11
M08-HX/jul-cc-pVTZ	20.96	12.17	17.76	17.71	22.15	4.49	4.70	4.44	2.86	2.29	16.47	7.47	13.32	14.84	19.86	0.24	0.22
M08-SO/jul-cc-pVTZ	21.99	13.17	18.65	18.51	21.99	5.08	5.24	5.39	3.04	1.46	16.90	7.93	13.26	15.47	20.54	0.70	0.76
M06-2X/jul-cc-pVTZ	19.07	10.68	15.94	15.78	19.88	3.11	3.38	3.21	1.39	0.46	15.96	7.29	12.73	14.39	19.42	1.10	1.07
M08-HX/jun-cc-pVTZ	20.99	12.25	17.82	17.68	22.20	4.52	4.72	4.46	2.81	2.30	16.47	7.53	13.36	14.86	19.90	0.25	0.23
M08-SO/jun-cc-pVTZ	22.07	13.35	18.80	18.55	22.09	5.14	5.32	5.45	3.02	1.49	16.93	8.03	13.35	15.53	20.59	0.77	0.84
M06-2X/jun-cc-pVTZ	19.12	10.74	16.01	15.78	19.92	3.09	3.37	3.20	1.33	0.44	16.02	7.36	12.81	14.46	19.48	1.08	1.05
M08-HX/maug-cc-pVTZ	21.06	12.34	17.84	17.94	22.29	4.61	4.81	4.50	3.09	2.38	16.45	7.52	13.34	14.85	19.90	0.29	0.26
M08-SO/maug-cc-pVTZ	22.10	13.39	18.79	18.75	22.14	5.25	5.39	5.49	3.28	1.55	16.85	8.00	13.30	15.47	20.58	0.81	0.88
M06-2X/maug-cc-pVTZ	19.16	10.76	15.98	15.97	19.94	3.18	3.43	3.19	1.53	0.47	15.97	7.33	12.79	14.44	19.47	1.04	1.01
M08-HX/MG3S	20.63	11.61	17.18	17.31	21.68	3.89	3.94	3.55	2.08	1.64	16.74	7.67	13.62	15.23	20.03	0.50	0.58
M08-SO/MG3S	21.04	12.31	17.47	17.45	21.21	4.64	4.66	4.58	2.34	0.79	16.41	7.65	12.89	15.11	20.42	0.37	0.27
M06-2X/MG3S	19.06	10.48	15.77	15.74	19.58	2.59	2.76	2.49	0.76	-0.02	16.47	7.72	13.27	14.99	19.60	1.36	1.34
CCSD(T)-F12a/jun-cc-pVTZ	20.32	12.38	17.57	17.47	21.72	4.52	4.76	4.43	2.91	1.90	15.80	7.62	13.14	14.56	19.82	0.00	0.00

[a]For consistent comparisons consistently, the same set of geometries (those obtained by M08-HX/MG3S) is used throughout this table. The lowest-energy structures for reactants, conventional transition states, and products are employed. Mean unsigned errors (MUEs) are calculated with respect to the CCSD(T)-F12a/jun-cc-pVTZ method. Barrier heights and energies of reaction are classical, i.e., zero-point-energy exclusive.

Table S7. Averaged generalized transmission coefficients[a] of reaction R1–R5 at various temperatures.

T/K	R1				R2				R3				R4				R5			
	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_3$	$\langle\gamma\rangle_4$	URE[b] (%)	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_3$	$\langle\gamma\rangle_4$	URE (%)	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_3$	$\langle\gamma\rangle_4$	URE (%)	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_3$	$\langle\gamma\rangle_4$	URE (%)	$\langle\gamma\rangle_1$	$\langle\gamma\rangle_3$	$\langle\gamma\rangle_4$	URE (%)
200	196.5	231.8	243.5	4.8	20.84	26.94	26.88	0.2	207.0	214.7	218.6	1.8	45.43	59.42	67.68	12.2	1.42	1.78	1.95	8.4
298.15	17.58	18.95	19.54	3.0	3.83	4.19	4.15	0.9	17.49	17.67	17.80	0.8	8.16	9.78	10.80	9.4	1.18	1.36	1.44	5.8
300	17.04	18.37	18.95	3.0	3.74	4.12	4.08	1.0	17.09	17.20	17.32	0.7	7.99	9.56	10.55	9.3	1.18	1.35	1.44	5.8
400	5.79	6.00	6.13	2.2	2.02	2.12	2.11	0.8	5.62	5.63	5.66	0.4	3.62	4.08	4.37	6.6	1.10	1.20	1.25	4.2
600	2.33	2.35	2.38	1.5	1.27	1.32	1.31	0.9	2.19	2.21	2.23	0.6	1.80	1.91	1.98	3.6	1.04	1.08	1.10	2.4
800	1.63	1.63	1.65	1.2	0.90	1.05	1.03	2.2	1.50	1.53	1.54	0.8	1.35	1.38	1.42	2.2	1.02	1.03	1.05	1.7
1000	1.36	1.35	1.37	1.2	0.73	0.90	0.87	3.3	1.23	1.27	1.29	1.1	1.16	1.17	1.18	1.5	1.01	1.01	1.02	1.5
1500	1.13	1.11	1.13	1.4	0.54	0.69	0.66	3.6	0.98	1.04	1.06	1.8	0.96	0.95	0.95	0.9	1.00	0.98	0.99	1.3
2000	1.06	1.03	1.05	1.7	0.45	0.59	0.57	3.6	0.87	0.95	0.97	2.5	0.87	0.85	0.85	0.9	1.00	0.97	0.98	1.3
2400	1.03	0.98	1.01	2.4	0.42	0.54	0.53	3.3	0.79	0.89	0.92	3.3	0.80	0.79	0.78	0.6	1.00	0.96	0.97	1.4
3000	1.01	0.95	0.98	2.9	0.38	0.50	0.48	3.7	0.63	0.78	0.83	5.6	0.68	0.68	0.66	3.4	1.00	0.95	0.97	1.5

[a] Generalized transmission coefficients averaged over the first p lowest-energy path(s) are denoted as $\langle\gamma\rangle_p$.

[b] Unsigned relative errors (UREs) re given by $\left|\langle\gamma\rangle_4 - \langle\gamma\rangle_3\right| / \langle\gamma\rangle_4$.

Table S8. Relative errors (%) of the computed MS-CVT/SCT branching ratios at various temperatures with respect to MP-CVT/SCT results.

T/K	R1	R2	R3	R4	R5
200	3.42	0.00	21.24	-14.10	-40.71
298.15	-1.35	0.00	7.12	-17.33	-34.05
300	-1.10	0.00	6.86	-17.35	-33.74
400	-0.47	-0.03	4.00	-12.82	-25.71
600	29.16	-1.22	27.23	18.73	7.41
800	32.69	-3.29	25.44	23.82	16.80
1000	30.46	-6.07	19.40	22.33	19.09
1500	22.00	-10.97	3.45	12.46	16.45
2000	20.40	-11.74	-5.13	6.99	16.61
2400	21.12	-12.52	-12.99	4.05	17.96
3000	52.97	9.74	-56.00	-48.11	49.67

Table S9. Locations of the variational transition state (in Å) of R1–R5 at 200, 298 and 1000 K, without treating torsional anharmonicity as a function of reaction coordinate *s*.

		200 K	298 K	1000 K
R1	Path 1	0.0059	0.0063	0.012
	Path 2	0.010	0.011	0.025
	Path 3	0.0016	0.0025	0.0075
	Path 4	0.0009	0.0018	0.0060
R2	Path 1	-0.021	-0.022	-0.21
	Path 2	-0.021	-0.024	-0.20
	Path 3	-0.019	-0.022	-0.19
	Path 4	-0.023	-0.026	-0.20
R3	Path 1	0.014	0.016	0.035
	Path 2	0.0093	0.0097	0.016
	Path 3	0.013	0.015	0.034
	Path 4	0.0055	0.0061	0.013
R4	Path 1	0.013	0.015	0.033
	Path 2	0.013	0.015	0.034
	Path 3	0.014	0.017	0.039
	Path 4	0.013	0.015	0.033
R5	Path 1	-0.0057	-0.0052	-0.0055
	Path 2	-0.0057	-0.0064	-0.018
	Path 3	-0.0018	-0.0024	-0.015
	Path 4	-0.0045	-0.0041	-0.0030

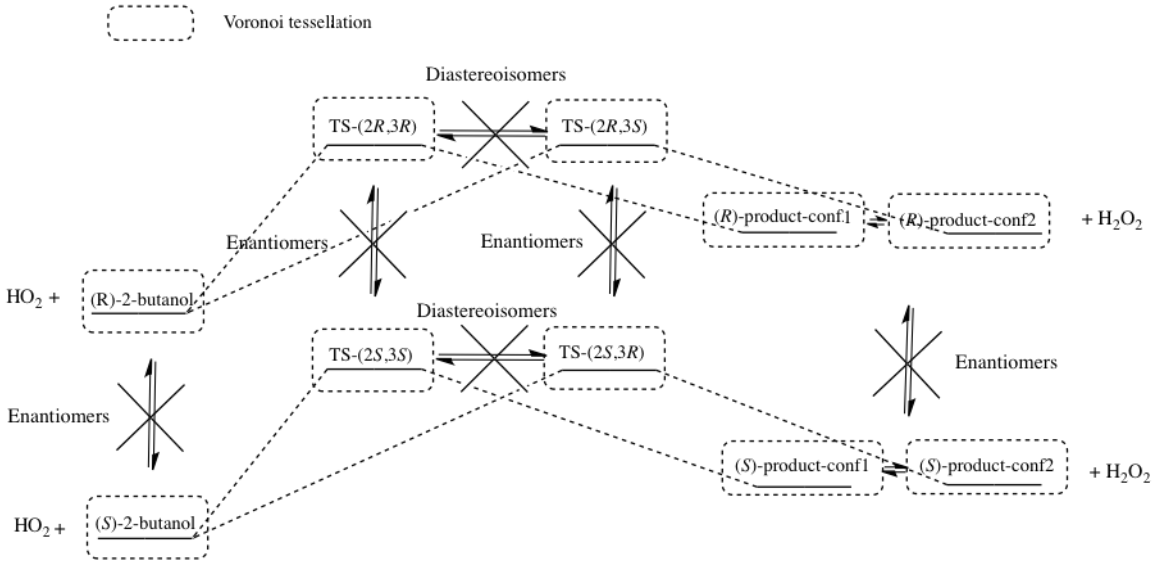

Fig S1. Schematic summary of the relation between various species for reaction R3. The arrows represent the conversion between two species by internal rotation (torsion); dotted lines connected species on the same potential energy surface along a reaction path.

Starting from (*R*)-2-butanol, the hydrogen abstraction from C-3 leads to a pair of transition structures, which are diastereomers, i.e. (2*R*, 3*R*) and (2*R*, 3*S*), and these two structures cannot be converted by torsions; starting from (*S*)-2-butanol, the hydrogen abstraction from C-3 leads to a pair of transition structures, which are diastereomers, i.e. (2*S*, 3*S*) and (2*S*, 3*R*), and these two structures cannot be converted via torsion either.

The following pairs of species are enantiomers and are not interconvertable by torsions: (*R*)-2-butanol and (*S*)-2-butanol; (2*R*, 3*R*) and (2*S*, 3*S*) TS3; (2*R*, 3*S*) and (2*S*, 3*R*) TS3; (*R*)–product–conformer *j* and (*S*)–product–conformer *j*.

The conformational-rotational-vibrational partition function of the transition state of R3 includes both diastereomers, (2*S*,3*R*) and (2*S*,3*S*), and their corresponding enantiomers, (2*R*,3*S*) and (2*R*,3*R*), are not included in the calculation because they are formed from (*R*)-2-butanol (whereas we computed the reaction rates only for (*S*)-2-butanol in the current work). The local periodicities for (2*S*,3*R*) and (2*S*,3*S*) transition structures are separately computed via independent Voronoi tessellation methods.