Electronic Supplementary Information

Multi-Structural Variational Transition State Theory. Kinetics of the 1,4-Hydrogen Shift Isomerization of the Pentyl Radical with Torsional Anharmonicity

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Table S1. Information used for the 1-pentyl radical partition function using the MS-RS-HO and MS-RS-T methods[a]

Torsion	$\overline{\omega}$	I	W	M
	Structure **1a**$^{+}$**g**$^{-}$**t** and **1a**$^{-}$**g**$^{+}$**g**$^{-}$ (U = 0)			
C(1)–C(2)	133	1.714	451	2
C(2)–C(3)	142	10.91	1458	3
C(3)–C(4)	99	15.98	1040	3
C(4)–C(5)	228	2.917	998	3
	Structure **1a**$^{-}$**g**$^{+}$**g**$^{+}$ (U = 0.077 kcal/mol)			
C(1)–C(2)	161	1.713	654	2
C(2)–C(3)	131	17.09	1923	3
C(3)–C(4)	108	18.38	1418	3
C(4)–C(5)	247	3.054	1228	3
	Structure **1a**$^{-}$**g**$^{+}$**g**$^{+}$ (U = 0.077 kcal/mol)			
C(1)–C(2)	157	1.713	625	2
C(2)–C(3)	132	15.88	1831	3
C(3)–C(4)	110	14.79	1188	3
C(4)–C(5)	254	3.057	1297	3
	Structure **1a**$^{-}$**tt** (U = 0.21 kcal/mol)			
C(1)–C(2)	126	1.67	38	6
C(2)–C(3)	110	14.45	1063	3
C(3)–C(4)	125	11.48	1079	3
C(4)–C(5)	229	3.039	976	3

[a]The units are cm^{-1} for torsional barrier heights W and frequencies $\overline{\omega}$. The unit is amu Å^{2} for internal moments of inertia. I, and the local periodicity M is unitless. See Ref. 15 for details of the method.

Table S2. Information used for the 2-pentyl radical partition function using the MS-RS-HO and MS-RS-T methods[a]

Torsion	$\overline{\omega}$	*I*	*W*	*M*
		Structure **2g$^-$t** and **2g$^+$t** (*U* = 0)		
C(1)–C(2)	216	3.064	943	3
C(2)–C(3)	145	10.934	1516	3
C(3)–C(4)	63	13.659	360	3
C(4)–C(5)	121	2.938	285	3
		Structure **2g$^-$t** (*U* = 0.022 kacl/mol)		
C(1)–C(2)	223	3.056	1001	3
C(2)–C(3)	116	18.821	1670	3
C(3)–C(4)	77	15.678	616	3
C(4)–C(5)	136	3.041	371	3
		Structure **2ta$^+$** (*U* = 0.16 kcal/mol)		
C(1)–C(2)	228	2.853	975	3
C(2)–C(3)	117	12.127	1101	3
C(3)–C(4)	62	10.777	275	3
C(4)–C(5)	122	2.823	278	3
		Structure **2g$^-$s** (*U* = 0.37 kcal/mol)		
C(1)–C(2)	238	3.073	1147	3
C(2)–C(3)	140	12.859	1667	3
C(3)–C(4)	61	15.235	378	3
C(4)–C(5)	98	3.026	190	3

[a] The units are cm^{-1} for torsional barrier heights W and frequencies $\overline{\omega}$. The unit is amu $Å^2$ for internal moments of inertia. *I*, and the local periodicity *M* is unitless. See Ref. 15 for details of the method.

Table S3. Transmission coefficients calculated using samll-curvature tunnling approximation at various temperatures based on the curve calculated by MCSI and *MC-TINKERATE* using the structures **TS−1**as transition state, **1a^{+}g^{-}t** and **2g^{-}t** as reactant and product wells

T (K)	transmission coefficient
200	1.17E+07
250	2.64E+04
298.15	9.06E+02
300	8.21E+02
400	2.94E+01
600	3.90E+00
1000	1.60E+00
1500	1.23E+00
2000	1.12E+00
2400	1.08E+00

Table S4. Cartesian coordinates (in Å) of 1-pentyl radical optimized by M06-2X/6-311+G(2df,2p)[a]

1a$^-$g$^+$t				**1a$^-$g$^+$g$^+$**			
C	−2.090217	−0.735153	0.176272	C	−1.775936	−0.722562	0.428132
H	−1.890012	−1.157083	1.151497	H	−1.940371	−0.341172	1.426444
H	−2.880158	−1.178716	−0.409878	H	−2.229248	−1.668268	0.173254
H	0.561679	−1.336352	−0.169595	H	1.829493	1.027429	0.937213
C	−1.461188	0.553652	−0.216065	C	−1.172098	0.151223	−0.611490
H	−1.494020	0.669283	−1.302901	H	−0.784989	−0.458521	−1.430837
H	−2.045618	1.392061	0.187797	H	−1.945519	0.787044	−1.063992
C	−0.015728	0.686351	0.269401	C	−0.066504	1.060927	−0.064265
H	0.346635	1.696684	0.063501	H	0.329289	1.666851	−0.883280
H	0.009059	0.563777	1.356907	H	−0.506150	1.756510	0.655248
C	0.925514	−0.326504	−0.373820	C	1.081526	0.304864	0.605367
H	0.890915	−0.203216	−1.459863	H	0.711655	−0.193826	1.504188
C	2.360633	−0.182186	0.117445	C	1.736577	−0.727165	−0.306624
H	2.416996	−0.327954	1.197167	H	2.047523	−0.274255	−1.250155
H	3.021788	−0.909240	−0.352756	H	2.617811	−1.163688	0.161761
H	2.748654	0.813799	−0.101277	H	1.049113	−1.541827	−0.536565

1a$^-$g$^+$g$^-$				**1a$^+$tg$^+$**			
C	1.649257	0.926046	0.130426	C	−2.456432	−0.179581	−0.111759
H	1.583309	1.175765	1.179846	H	−2.852523	0.821850	−0.202462
H	2.165157	1.617043	−0.518704	H	−3.153839	−1.002368	−0.147555
H	−1.371446	−0.792287	−1.222697	H	1.890815	1.467124	−0.101363
C	1.279227	−0.438214	−0.331867	C	−1.035660	−0.389826	0.266922
H	1.117920	−0.437952	−1.413982	H	−0.937396	−0.440286	1.362798
H	2.127278	−1.117007	−0.164333	H	−0.699265	−1.363212	−0.097898
C	0.049020	−1.030002	0.369053	C	−0.113274	0.717223	−0.246026
H	0.072249	−2.116307	0.264445	H	−0.118349	0.704906	−1.339678
H	0.117379	−0.820457	1.441096	H	−0.529152	1.682366	0.054400
C	−1.290695	−0.523522	−0.165771	C	1.323192	0.607675	0.260257
H	−2.090942	−1.061830	0.346832	H	1.324732	0.674759	1.351625
C	−1.518233	0.976621	−0.006241	C	2.024868	−0.676293	−0.172615
H	−0.817645	1.555522	−0.607230	H	1.983439	−0.792235	−1.257210
H	−2.527942	1.250157	−0.312252	H	3.073198	−0.671639	0.123490
H	−1.386766	1.281778	1.033380	H	1.562177	−1.556453	0.273184

1a$^+$tt				**1a$^+$tg$^-$**			
C	2.576312	−0.345454	−0.021135	C	2.455792	−0.165835	−0.122534
H	2.570542	−1.343341	0.393623	H	2.686850	0.401239	−1.012945
H	3.527248	0.074228	−0.311395	H	3.261246	−0.698737	0.359197
H	−1.180728	1.109833	0.959874	H	−1.343256	0.603143	1.381560
C	1.347607	0.488063	0.020354	C	1.042552	−0.380574	0.282223
H	1.332306	1.095784	0.937708	H	0.685868	−1.342151	−0.111838
H	1.358072	1.211149	−0.800890	H	0.974155	−0.473484	1.371547
C	0.060484	−0.332466	−0.035161	C	0.112336	0.734644	−0.195096
H	0.049805	−0.921863	−0.956332	H	0.513880	1.691784	0.145352
H	0.058870	−1.051648	0.789753	H	0.127478	0.763415	−1.289150
C	−1.197979	0.523557	0.037317	C	−1.328821	0.588550	0.288381
H	−1.189188	1.244614	−0.784297	H	−1.898576	1.460958	−0.037162
C	−2.474304	−0.307216	−0.021117	C	−2.018045	−0.676723	−0.214172
H	−2.513643	−1.015953	0.807216	H	−1.557730	−1.575673	0.194881
H	−3.364476	0.318537	0.031297	H	−3.070141	−0.690234	0.068228
H	−2.521528	−0.880239	−0.948106	H	−1.962666	−0.740627	−1.302482

1stg$^+$				**1stt**			
C	2.457274	−0.214481	0.087058	C	2.585902	−0.315573	0.000003
H	3.081579	0.537444	−0.372739	H	2.993955	−0.697730	0.923780
H	2.840235	−0.716634	0.962526	H	2.993483	−0.698457	−0.923686
H	−1.881413	1.463105	0.218984	H	−1.190100	1.173774	0.874709
C	1.039001	−0.372190	−0.327141	C	1.350864	0.510298	−0.000034
H	0.953220	−0.301652	−1.416174	H	1.332810	1.161804	0.877660
H	0.678589	−1.362172	−0.043426	H	1.332780	1.161677	−0.877827
C	0.119708	0.697840	0.292914	C	0.063878	−0.334168	0.000031
H	0.134905	0.589094	1.381031	H	0.065809	−0.989473	−0.875400
H	0.537076	1.683041	0.073611	H	0.065806	−0.989339	0.875561
C	−1.321039	0.630452	−0.210753	C	−1.199804	0.518326	−0.000039
H	−1.329082	0.780145	−1.293763	H	−1.190101	1.173633	−0.874892
C	−2.026270	−0.678975	0.129559	C	−2.470759	−0.322863	0.000031
H	−1.976713	−0.876963	1.201885	H	−2.510034	−0.965752	0.880373
H	−3.077076	−0.645890	−0.155863	H	−3.364855	0.299642	−0.000017
H	−1.573363	−1.525394	−0.385895	H	−2.510038	−0.965892	−0.880210

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[a] The coordinates for mirror image structures are only given for only one of the two structures in each case.

Table S5. Cartesian coordinates (in Å) of 2-pentyl radical optimized by M06-2X/6-311+G(2df,2p)[a]

2g⁻t				**2g⁻g⁻**			
C	1.950205	−0.808906	0.158730	C	1.767160	−0.746624	0.323183
H	1.922904	−0.955072	1.239877	H	2.214858	−0.226103	1.171494
H	2.980578	−0.936145	−0.171453	H	2.553121	−1.310498	−0.177909
H	1.349026	−1.597425	−0.294675	H	1.042176	−1.458260	0.720509
C	1.410558	0.568856	−0.209597	C	1.098308	0.242430	−0.623811
H	2.043461	1.341200	0.230667	H	1.845452	0.916312	−1.046999
H	1.459544	0.707780	−1.292752	H	0.654054	−0.294258	−1.465556
C	−0.032834	0.773492	0.251371	C	0.009414	1.079659	0.071155
H	−0.093281	0.633944	1.337252	H	0.467072	1.665743	0.870378
H	−0.321361	1.820929	0.077121	H	−0.383639	1.796500	−0.661103
C	−1.003816	−0.135509	−0.417615	C	−1.111843	0.260421	0.612387
H	−0.805142	−0.425108	−1.442572	H	−1.276883	0.206726	1.678354
C	−2.374310	−0.317880	0.128831	C	−1.897566	−0.621241	−0.292228
H	−2.984814	0.586980	0.006142	H	−1.356678	−1.543537	−0.542954
H	−2.904741	−1.132625	−0.361475	H	−2.845922	−0.918548	0.152553
H	−2.344991	−0.524777	1.201550	H	−2.106446	−0.121954	−1.242882
2tg⁻				**2ta⁺**			
C	−2.395793	−0.202439	0.134255	C	−2.515692	−0.294896	−0.004411
H	−2.429239	−0.358718	1.213393	H	−2.534775	−1.041009	−0.800078
H	−3.056700	−0.933016	−0.330889	H	−3.403192	0.327964	−0.109083
H	−2.798521	0.790992	−0.068082	H	−2.588320	−0.824654	0.946535
C	−0.968945	−0.324268	−0.385950	C	−1.238222	0.532599	−0.068151
H	−0.587915	−1.329966	−0.194524	H	−1.191891	1.075751	−1.014666
H	−0.950408	−0.185490	−1.469289	H	−1.246224	1.288151	0.721325
C	−0.024386	0.702098	0.265038	C	0.019441	−0.319865	0.075366
H	−0.418262	1.704317	0.081782	H	−0.040256	−0.882206	1.020999
H	−0.054601	0.543923	1.349955	H	0.032857	−1.088396	−0.707651
C	1.380569	0.599859	−0.215616	C	1.283308	0.462521	0.024817
H	1.706937	1.241166	−1.023143	H	1.251138	1.510643	0.293783
C	2.219591	−0.572915	0.150879	C	2.597175	−0.228452	−0.052063
H	2.005064	−1.447924	−0.476718	H	2.595115	−0.991613	−0.834921
H	3.282987	−0.361294	0.042181	H	3.412609	0.464029	−0.253787
H	2.034437	−0.877996	1.183699	H	2.836876	−0.750099	0.884197

2g$^+$s				**2g$^+$p**			
C	−1.585309	1.025572	−0.000902	C	1.680578	−0.804622	−0.278252
H	−0.853489	1.543835	0.620008	H	2.091971	−0.469789	−1.23161
H	−2.578107	1.345027	0.313826	H	2.477828	−1.30518	0.270854
H	−1.438570	1.353031	−1.031908	H	0.91052	−1.543322	−0.495665
C	−1.421480	−0.485369	0.114152	C	1.128144	0.382599	0.506363
H	−1.566745	−0.793343	1.152301	H	1.941781	1.086713	0.687418
H	−2.192014	−0.988855	−0.473451	H	0.782188	0.058249	1.490759
C	−0.037725	−0.964697	−0.357162	C	−0.006896	1.12013	−0.213774
H	−0.022764	−2.059185	−0.322589	H	0.261709	1.201692	−1.278979
H	0.093666	−0.683026	−1.406410	H	−0.055138	2.152228	0.14351
C	1.084514	−0.408162	0.449965	C	−1.367145	0.518123	−0.072751
H	1.170163	−0.704981	1.48673	H	−2.205491	1.14246	−0.352804
C	2.042935	0.576174	−0.119170	C	−1.622601	−0.936856	0.109124
H	1.52501	1.462251	−0.504969	H	−1.459273	−1.506427	−0.816107
H	2.774101	0.9095	0.614683	H	−2.65218	−1.116388	0.41534
H	2.59114	0.154639	−0.969521	H	−0.96639	−1.376475	0.863028

[a] The coordinates for mirror image structures are only given for only one of the two structures in each case.

Table S6. Cartesian coordinates (in Å) of the transition state of 1,4-hydrogen shift reaction of 1-pentyl radical optimized by M06-2X/6-311+G(2df,2p)[a]

TS−1				**TS−3**			
C	1.406518	1.050028	−0.117361	C	1.398554	−0.960407	0.232897
H	1.348372	1.395515	−1.146628	H	1.996920	−0.876943	1.136269
H	1.988121	1.705572	0.520649	H	1.555385	−1.893252	−0.296807
H	0.078916	1.029758	0.286810	H	0.100933	−0.893976	0.720091
C	1.542812	−0.448821	0.060178	C	1.242701	0.314910	−0.571656
H	2.286040	−0.900601	−0.597904	H	2.168960	0.883074	−0.663446
H	1.839137	−0.671211	1.086984	H	0.912308	0.077680	−1.583687
C	0.124362	−0.99368	−0.192817	C	0.144392	1.111103	0.166846
H	−0.072742	−1.002846	−1.268605	H	0.583365	1.616922	1.028422
H	−0.010727	−2.013313	0.171739	H	−0.313531	1.875642	−0.464788
C	−0.798336	0.014054	0.468786	C	−0.849526	0.062143	0.638795
H	−0.819679	−0.071686	1.555256	H	−1.269941	0.211969	1.629364
C	−2.136859	0.289150	−0.157029	C	−1.841335	−0.422727	−0.387383
H	−2.781938	−0.594990	−0.120385	H	−1.337241	−0.740430	−1.302105
H	−2.662108	1.098320	0.349484	H	−2.426066	−1.264341	−0.018204
H	−2.024371	0.561093	−1.207945	H	−2.539807	0.373518	−0.662102

[a] The coordinates for mirror image structures are only given for only one of the two structures in each case.

Table S7. The ratio of the multi-structural torsional anharmonicity factors calculated with the scaling factor over that without the scaling factor[a]

T (K)	R_R	R_{TS}	R_P
200	1.00	1.01	1.01
250	1.00	1.01	1.01
298.15	1.00	1.01	1.00
300	1.00	1.01	1.00
400	1.00	1.01	1.00
600	0.99	1.00	0.98
1000	0.97	0.99	0.96
1500	0.96	0.99	0.94
2000	0.94	0.98	0.93
2400	0.94	0.98	0.93

[a] The ratio is defined $R_X = (F^X_{\text{MS-AS-T}})_{\text{scale}} / (F^X_{\text{MS-AS-T}})_{\text{noscale}}$, where X = ‡, R, and P.

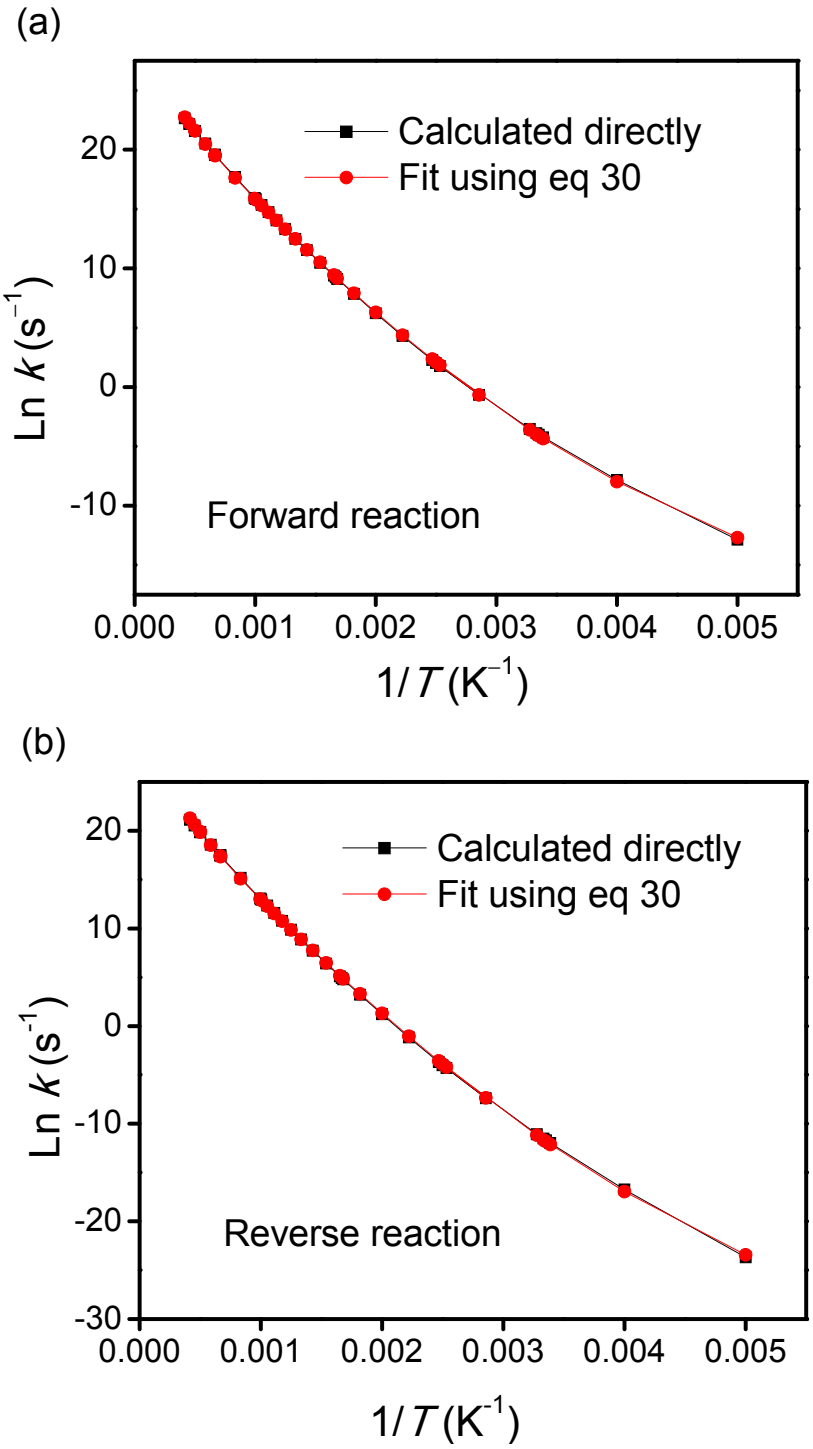

Figure S1. Plot of the calculated MS-VTST (a) forward and (b) reverse rate constants for the 1,4-hydrogen shift isomerization reaction of 1-pentyl radical with rate constant fitting curve using the eq 30. The fitting parameters are $A = 1.06\times10^{8}$ s^{-1}, $n = 3.2897$, $E = 11.436$ kcal/mol, and $T_0 = 185.34$ K for the forward reaction; and; $A = 8.81\times10^{6}$ s^{-1}, $n = 4.01577$, $E = 13.865$ kcal/mol, and $T_0 = 165.90$ K for the reverse reaction.