Electronic Supplementary Information

Kinetics Study on Hydrogen Abstraction Reactions of Cyclopentane by Hydrogen, Methyl, and Ethyl Radicals

Wenqi Chen[2,‖], Xuan Guo,[1,2,‖] Lifang Chen,[1] Ruiming Zhang,[2] Yan Li,[2] Haisong Feng,[1] Xuefei Xu[2,*] and Xin Zhang,[1,*]

[1]*State Key Laboratory of Chemical Resource Engineering, Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China*
[2]*Center for Combustion Energy, Department of Energy and Power Engineering, and Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China*

[*]E-mail addresses: xuxuefei@mail.tsinghua.edu.cn (X. X);
zhangxin@mail.buct.edu.cn (X. Z)
[‖]These authors contributed equally.

Contents

Quartic anharmonicity correction

As we mentioned in the manuscript, two *half-chair* (HC) conformers of cyclopentane are interconverted through a low-frequency out-of-plane bending mode, which leads to a double-well potential with a quartic anharmonicity. The *envelope* (EN) conformation is the local maximum of the double-well potential. By using a quadratic-quartic model, the double-well potential can be expressed as:

$$V = \frac{1}{2}kq_m^2 + Aq_m^4 \tag{1}$$

where k and A are fitting parameters; q_m is the coordinate of the bending motion within a mass-scaled coordinate system in which the equivalent mass is set equal to 1amu. The quadratic-quartic formulas are fitted by adopting structural parameters, for example, bending mode frequencies and intrinsic reaction coordinates.

To get the parameter k and A, firstly we calculate the first and second derivative of potential V:

$$\frac{\partial V}{\partial q_m} = kq_m + 4Aq_m^3 \tag{2}$$

$$\frac{\partial^2 V}{\partial q_m^2} = k + 12Aq_m^2 \tag{3}$$

The first derivative of V is zero when $q_m = \pm q_{HC}$ or $q_m = q_{EN} = 0$. Thus, we have:

$$\left.\frac{\partial V}{\partial q_m}\right|_{q_m = q_{HC}} = kq_{HC} + 4Aq_{HC}^3 = 0 \tag{4}$$

The solution to equation (4) is:

$$q_{HC} = \frac{1}{2}\sqrt{-\frac{k}{A}} \tag{5}$$

Hence, the frequencies of this bending mode at the EN and HC conformers can be expressed as:

$$\omega_{\mathrm{EN}} = \sqrt{\frac{1}{\mu}\left.\frac{\partial^2 V}{\partial q_m^2}\right|_{q_m = q_{EN}}} = \sqrt{\frac{k}{\mu}} \tag{6}$$

$$\omega_{\mathrm{HC}} = \sqrt{\frac{1}{\mu}\frac{\partial^2 V}{\partial q_m^2}\bigg|_{q_m = q_{HC}}} = \sqrt{\frac{-2k}{\mu}} \tag{7}$$

where μ is set to 1 amu.

We have obtained the frequency of $\omega_{\mathrm{EN}} = 6.29i$ cm^{-1} / $\omega_{\mathrm{HC}} = 42.89$ cm^{-1} by the M08-HX/MG3S method and $\omega_{\mathrm{EN}} = 12.43i$ cm^{-1} / $\omega_{\mathrm{HC}} = 24.06$ cm^{-1} by the M06-2X/jun-cc-pVTZ method, respectively. Take these frequencies to equations (6) and (7) we can get the second-order force constant *k*. We take the average of the *k* values calculated with the two equations as the final *k*, which is -7.16×10^{-4} J/m^2 (-3.32×10^{-4} J/m^2) by the M08-HX/MG3S (M06-2X/jun-cc-pVTZ) method.

Then we calculate the q_{HC} using Chen's method.[1] We note that to calculate this distance correctly we need to make the origin and orientation consistent between the EN and HC structures. The calculated q_{HC} is 0.294 Å or 0.540 Å by the M08-HX/MG3S method or by the M06-2X/jun-cc-pVTZ method.

We bring these results into equation (5) and get the fourth-order force constant *A,* which is 2.07×10^{17} J/m^4 or 2.85×10^{16} J/m^4 by the M08-HX/MG3S method or by the M06-2X/jun-cc-pVTZ method.

Once the quadratic-quartic potential is fitted, we use the Fourier Grid Hamiltonian (FGH)[2] method to solve the 1D Schrödinger equation:

$$-\frac{\hbar^2}{2\mu}\frac{d\psi}{dx} + (\frac{1}{2}kx^2 + Ax^4)\psi = \varepsilon_i\psi \tag{8}$$

Then, the partition function of this low-frequency bending mode with the quartic anharmonic correction is computed by:

$$Q_{\mathrm{QQ}} = \sum_i \exp(-\frac{\varepsilon_i}{k_B T}) \tag{5}$$

[1] C. Zhixing, Rotation Procedure in Intrinsic Reaction Coordinate Calculations. *Theoret. Chim. Acta* 1989, **75** (6), 481–484.
[2] C. C. Marston; G. G. Balint-Kurti, *J. Chem. Phys.*, 1989, **91**(6): 3571-3576.

Table S1 The classical reaction energies ΔV, forward ($V_F^{\neq}$) and reverse ($V_R^{\neq}$) barrier heights (in kcal/mol) excluding zero-point energy for the R1 reaction. The used geometries were optimized by the M06-2X/MG3S method.

Method	Basis set	R1 (with H radical)		
		$V^{\ddagger}$		ΔV
		Forward	Reverse	
M06-2X	MG3S	9.14	14.93	-5.79
	jun-cc-pVTZ	9.03	14.87	-5.83
	jul-cc-pVTZ	9.01	14.85	-5.83
M05-2X	MG3S	9.95	15.10	-5.15
	jun-cc-pVTZ	9.84	15.00	-5.17
	jul-cc-pVTZ	9.82	14.98	-5.17
M06	MG3S	7.66	14.63	-6.97
	jun-cc-pVTZ	7.50	14.28	-6.78
	jul-cc-pVTZ	7.46	14.22	-6.76
M06L	MG3S	7.17	12.34	-5.16
	jun-cc-pVTZ	6.96	11.92	-4.96
	jul-cc-pVTZ	6.94	11.88	-4.94
M08-HX	MG3S	8.10	13.30	-5.20
	jun-cc-pVTZ	7.97	13.24	-5.28
	jul-cc-pVTZ	7.97	13.21	-5.24
MPW1K	MG3S	7.28	13.52	-6.24
	jun-cc-pVTZ	7.16	13.38	-6.22
	jul-cc-pVTZ	7.14	13.37	-6.23
CCSD(T)-F12b	jul-cc-pVTZ	8.35	13.74	-5.39

Table S2 The classical reaction energies ΔV, forward ($V_F^{\neq}$) and reverse ($V_R^{\neq}$) barrier heights (in kcal/mol) excluding zero-point energy for the R2 and R3 reactions. The used geometries were optimized by the M06-2X/MG3S method.

Method	Basis set	R2 (CH_3)			R3 (CH_2CH_3)		
		$V‡$		ΔV	$V‡$		ΔV
		Forward	Reverse		Forward	Reverse	
M06-2X	MG3S	11.38	20.79	-9.42	12.67	17.98	-5.30
	jun-cc-pVTZ	11.58	20.98	-9.40	13.00	18.31	-5.31
	jul-cc-pVTZ	11.56	20.97	-9.41	12.98	18.28	-5.31
M05-2X	MG3S	11.59	21.19	-9.59	13.51	18.85	-5.35
	jun-cc-pVTZ	11.81	21.29	-9.48	13.80	19.11	-5.31
	jul-cc-pVTZ	11.79	21.28	-9.49	13.78	19.08	-5.31
M06	MG3S	10.59	21.87	-11.28	12.46	18.80	-6.34
	jun-cc-pVTZ	10.71	21.88	-11.17	12.74	18.95	-6.21
	jul-cc-pVTZ	10.65	21.79	-11.14	12.65	18.85	-6.20
M06L	MG3S	9.17	21.80	-12.63	11.63	18.63	-7.01
	jun-cc-pVTZ	9.15	21.66	-12.51	11.77	18.64	-6.87
	jul-cc-pVTZ	9.06	21.52	-12.46	11.64	18.52	-6.87
M08-HX	MG3S	12.51	21.58	-9.07	13.48	18.63	-5.15
	jun-cc-pVTZ	12.89	21.91	-9.02	14.08	19.18	-5.11
	jul-cc-pVTZ	12.85	21.91	-9.06	14.05	19.16	-5.12
MPW1K	MG3S	12.93	22.92	-9.99	15.72	21.50	-5.78
	jun-cc-pVTZ	13.00	22.92	-9.92	15.90	21.62	-5.72
	jul-cc-pVTZ	13.00	22.91	-9.91	15.89	21.60	-5.72
CCSD(T)-F12b	jul-cc-pVTZ	12.12	20.51	-8.39	13.03	17.95	-4.92

Table S3. The calculated anharmonic factors and rate constants (in $cm^3molecule^{-1}s^{-1}$) of cyclopentane reaction with three radials

T(K)	H			CH_3			CH_2CH_3		
	F_{act}^{MS-T}	F_{QQ}	$k^{\text{MS-CVT/SCT}}$	F_{act}^{MS-T}	F_{QQ}	$k^{\text{MS-CVT/SCT}}$	F_{act}^{MS-T}	F_{QQ}	$k^{\text{MS-CVT/SCT}}$
150	1.00	0.60	8.55E-17	2.04	0.60	1.55E-23	6.44	0.65	7.28E-27
200	1.00	0.65	4.81E-16	1.94	0.65	4.97E-22	7.01	0.70	1.31E-24
230	1.00	0.67	1.24E-15	1.88	0.67	3.34E-21	7.29	0.73	1.57E-23
260	1.00	0.69	2.86E-15	1.82	0.69	1.84E-20	7.54	0.75	1.29E-22
298.15	1.00	0.71	7.19E-15	1.75	0.71	1.20E-19	7.82	0.78	1.20E-21
330	1.00	0.73	1.39E-14	1.70	0.73	4.56E-19	8.01	0.80	5.70E-21
360	1.00	0.75	2.40E-14	1.65	0.75	1.38E-18	8.18	0.81	2.04E-20
390	1.00	0.77	3.90E-14	1.61	0.77	3.64E-18	8.32	0.83	6.25E-20
420	1.00	0.78	6.08E-14	1.57	0.78	8.65E-18	8.45	0.85	1.69E-19
450	1.00	0.79	9.08E-14	1.53	0.79	1.88E-17	8.57	0.86	4.11E-19
500	1.00	0.81	1.64E-13	1.47	0.81	5.83E-17	8.71	0.88	1.49E-18
600	1.00	0.85	4.31E-13	1.37	0.85	3.56E-16	8.94	0.93	1.17E-17
800	1.00	0.92	1.71E-12	1.22	0.92	4.46E-15	9.14	1.00	2.01E-16
1000	1.00	0.97	4.58E-12	1.11	0.97	2.47E-14	9.13	1.06	1.37E-15
1200	1.00	1.02	9.64E-12	1.02	1.02	8.76E-14	9.01	1.12	5.57E-15
1400	1.00	1.06	1.75E-11	0.96	1.06	2.36E-13	8.85	1.17	1.66E-14
1600	1.00	1.09	2.86E-11	0.90	1.09	5.29E-13	8.68	1.22	4.02E-14
1800	1.00	1.13	4.33E-11	0.85	1.13	1.03E-12	8.49	1.26	8.40E-14
2000	1.00	1.16	6.20E-11	0.81	1.16	1.84E-12	8.30	1.31	1.57E-13
2200	1.00	1.19	8.45E-11	0.78	1.19	3.03E-12	8.10	1.35	2.70E-13
2400	1.00	1.22	1.11E-10	0.74	1.22	4.70E-12	7.94	1.39	4.37E-13
2600	1.00	1.25	1.42E-10	0.72	1.25	6.99E-12	7.76	1.44	6.67E-13
2800	1.00	1.27	1.78E-10	0.69	1.27	9.97E-12	7.60	1.47	9.79E-13
3000	1.00	1.30	2.18E-10	0.67	1.30	1.37E-11	7.44	1.51	1.38E-12

Table S4. Rate constants (in $cm^3molecule^{-1}s^{-1}$) of several experimental studies

Handford-Styring and Walker[3] (With hydrogen radical)

T(K)	Rate constant
753	3.06E-12

Zhang *et al.*[4] (with methyl and ethyl radicals)

Methyl radical		Ethyl radical	
T(K)	Rate constant	T(K)	Rate constant
650	4.21E-16	650	1.59E-16
670	5.13E-16	670	1.99E-16
690	6.19E-16	690	2.45E-16
710	7.39E-16	710	2.98E-16
730	8.74E-16	730	3.59E-16
750	1.02E-15	750	4.28E-16
770	1.19E-15	770	5.05E-16

[3] S. M. Handford-Styring and R. W. Walker, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 1431–1438.
[4] H. X. Zhang, S. I. Ahonkhai, M. H. Back. *Can. J. Chem.*, 1989, **67**, 1541-1549.

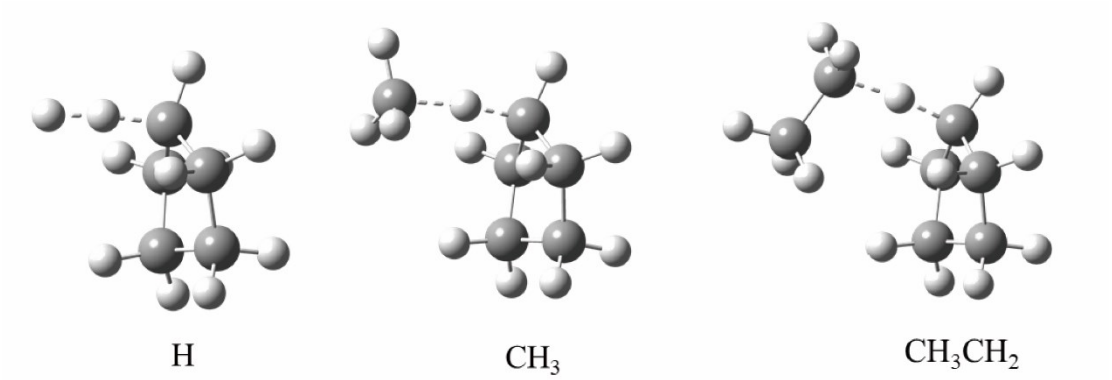

Figure S1. Lowest-energy structures of transition states for cyclopentane reactions with the three radicals.

Cartesian coordinates of optimized structures.

We use the best performing KS model chemistry for each system to optimize the structure, that is, the M08-HX/MG3S for reaction R1 (hydrogen abstraction reaction by H radicals) and for reaction R2 (hydrogen abstraction reaction by CH_3), and the M06-2X/jun-cc-pVTZ for R3 (hydrogen addition reaction by CH_3CH_2). Only one structure is given for each pair of enantiomers. (Unit: Angstrom)

TS_{R1} (H)

C	-1.204538126	0.279516186	-0.115250042
C	-0.064195021	1.296338207	-0.014231164
C	-0.579341665	-1.087563495	-0.340402261
C	0.778817145	-0.953676888	0.353544908
C	1.229597314	0.453611267	-0.053279153
H	-2.045506080	0.546875582	-0.756254086
H	-1.721742739	0.212231298	1.021568742
H	0.634999999	-1.001062594	1.440639022
H	2.017281354	0.856859677	0.587749762
H	1.491470201	-1.734126016	0.075485018
H	1.624002114	0.424512339	-1.075569163
H	-0.136528789	1.859275377	0.923697939
H	-1.194774805	-1.904618988	0.048327641
H	-0.434649788	-1.267073647	-1.414824168
H	-0.099366787	2.032335388	-0.822595979
H	-2.044321253	0.114985454	1.991387123

TS_{R2} (CH_3)

C	0.367796709	0.275049400	0.930852415
C	-0.488164425	1.293756351	0.174174458
C	-0.262103608	-1.093357456	0.726674136
C	-0.937808450	-0.949578410	-0.640229857
C	-1.549880786	0.453555703	-0.568255930
H	0.656265515	0.536639707	1.949599583
H	1.481691535	0.202007594	0.299127494
H	-0.172585339	-0.982241876	-1.427284705
H	-1.808824677	0.863540540	-1.547742910
H	-1.670081810	-1.732634795	-0.853113631
H	-2.472164763	0.413346699	0.023002277
H	0.127625381	1.858261473	-0.537907615
H	0.470713217	-1.906433537	0.768703510
H	-1.018843479	-1.295597888	1.497829324
H	-0.943311364	2.031755410	0.841643185
C	2.609820699	0.024180225	-0.534347840

H	3.460802804	0.181577648	0.122348426
H	2.501269511	-0.996880506	-0.892283860
H	2.487271715	0.783728439	-1.302050676

TS_{R3} (CH_2CH_3)-1 (The lowest-energy structure, whose energy is taken as the zero of energy for other conformers, so E = 0.00 kcal/mol)

C	-0.26649294	0.86437882	0.74465985
C	-0.93755781	1.14550676	-0.59988488
C	-0.73076085	-0.50685189	1.22163974
C	-1.28146273	-1.17410775	-0.04354499
C	-1.93385060	-0.00979500	-0.79087183
H	-0.31546293	1.66128565	1.48197369
H	1.01487979	0.76370684	0.51574789
H	-0.45814590	-1.57532267	-0.63888686
H	-2.13764955	-0.22836495	-1.83820662
H	-1.96959559	-1.99109458	0.16828596
H	-2.88339840	0.23943595	-0.31206593
H	-0.19387396	1.12941576	-1.40348071
H	0.06923699	-1.08056677	1.69415664
H	-1.52993468	-0.40402892	1.96128959
H	-1.41702870	2.12287556	-0.63576387
C	2.36176851	-0.74230284	-0.60702387
H	1.97388159	-1.57800867	-0.02286900
H	3.37596230	-1.00732679	-0.91930681
H	1.75655563	-0.65957986	-1.51101668
C	2.33594151	0.53678989	0.18674496
H	2.60386046	1.43326670	-0.36612892
H	2.82520541	0.49260090	1.15595776

TS_{R3} (CH_2CH_3)-2 (Relative energy E = 0.15 kcal/mol)

C	-0.30677667	1.02704989	0.78176422
C	-1.00406100	1.19479187	-0.56790196
C	-0.74973915	-0.30299808	1.36324383
C	-1.02119415	-1.13989005	0.11183420
C	-1.72868782	-0.14585460	-0.81418437
H	-0.31635966	1.88427965	1.44977518
H	0.96048882	0.86047155	0.50071767
H	-0.06939766	-1.44720594	-0.33061564
H	-1.71336918	-0.44921653	-1.85962576
H	-1.60668362	-2.03723800	0.30584640
H	-2.77447812	-0.06102979	-0.51318180
H	-0.27207201	1.39058190	-1.35592838

H	-0.00850516	-0.74442111	2.03041499
H	-1.67582649	-0.18655350	1.93659420
H	-1.69783063	2.03569659	-0.57255505
C	2.72180773	-0.52601008	1.09480057
H	2.63438239	-0.21400290	2.13646870
H	3.76740301	-0.79894980	0.92521225
H	2.12710722	-1.43154677	0.96684745
C	2.26845601	0.56288421	0.15921481
H	2.18846977	0.27474057	-0.88609396
H	2.77152744	1.51859265	0.27962796

TS_{R3} (CH_2CH_3)-3 (Relative energy E = 0.20 kcal/mol)

C	-0.31600103	0.94686202	0.93450705
C	-1.03117173	1.36933891	-0.34486985
C	-0.75013051	-0.47112330	1.24668952
C	-0.94320465	-1.06961958	-0.14819388
C	-1.62191709	0.06369944	-0.92870251
H	-0.31618783	1.65919864	1.75551932
H	0.95367550	0.82238412	0.62567025
H	0.03574016	-1.29027680	-0.58088507
H	-1.47393706	-0.01967408	-2.00434946
H	-1.52242564	-1.99166776	-0.14966741
H	-2.69715359	0.03184303	-0.74735407
H	-0.34015205	1.84340370	-1.04457515
H	-0.02295848	-1.01352830	1.85253971
H	-1.70121107	-0.47685474	1.79009365
H	-1.81513319	2.10122684	-0.14369584
C	2.28853228	0.83243367	-1.27787268
H	1.52993806	0.25630395	-1.81149371
H	3.25788568	0.56951465	-1.71143931
H	2.11468451	1.88749823	-1.49091543
C	2.24422477	0.55744450	0.20216832
H	2.85443170	1.21366710	0.81649030
H	2.36388162	-0.48703978	0.48092682

TS_{R3} (CH_2CH_3)-4 (Relative energy E = 0.26 kcal/mol)

C	-0.24766856	0.74375522	0.97222580
C	-0.81173355	1.26194254	-0.35114389
C	-0.84860900	-0.62905409	1.22909178
C	-1.21853413	-1.11551915	-0.17435577
C	-1.75968972	0.15101265	-0.84097432
H	-0.24759241	1.43820351	1.80842398

H	1.01927320	0.52328080	0.75975596
H	-0.31606173	-1.44900402	-0.69318885
H	-1.80657532	0.08104260	-1.92660360
H	-1.92934354	-1.94040031	-0.17367990
H	-2.77161527	0.34223623	-0.47790752
H	-0.00402731	1.41242037	-1.07429734
H	-0.16243953	-1.29856883	1.75022599
H	-1.75200381	-0.54787961	1.84175890
H	-1.31866480	2.22056662	-0.24454590
C	2.91768808	1.74261892	0.37857964
H	2.39752430	2.35191708	-0.36187466
H	3.97821869	1.74234799	0.11261637
H	2.82405287	2.24243448	1.34315289
C	2.34914800	0.34983527	0.43211137
H	2.72713310	-0.28164596	1.23140805
H	2.30551233	-0.17424822	-0.51931902

MS-T internal coordinates for TS -R3 (CH_2CH_3)

$INTDEF

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