Molecular dynamics calculation of activation volumes

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Supplementary Information

Force Field Parameters for Transition States
(Only parameters different from OPLS are listed)

Tables 1-4. Cyclopentadiene Dimerization (Fig. 1)

Table 1. Charges and Lennard-Jones Parameters

Atom #	Atom Type	q (a.u.)	σ (nm)	ε (kJ mol^{-1})
3	C	-0.087	0.352	0.297
4	H	0.087	0.246	0.126
14	C	-0.087	0.352	0.297
15	H	0.087	0.246	0.126

Table 2. Bond Parameters

Atom #s	Bond Type	Equilibrium Length (nm)	Force Constant (kJ mol^{-1} nm^{-2})
1-19	C-C	0.28960	1200
8-12	C-C	0.28960	1200
1-3	C-C	0.14183	360568
3-5	C-C	0.15262	237914
5-8	C-C	0.15052	258027
8-10	C-C	0.13695	435513
10-1	C-C	0.14232	354108
12-14	C-C	0.14183	360568
14-16	C-C	0.15262	238280
16-19	C-C	0.15052	258225
19-21	C-C	0.13695	434677
21-12	C-C	0.14222	354926

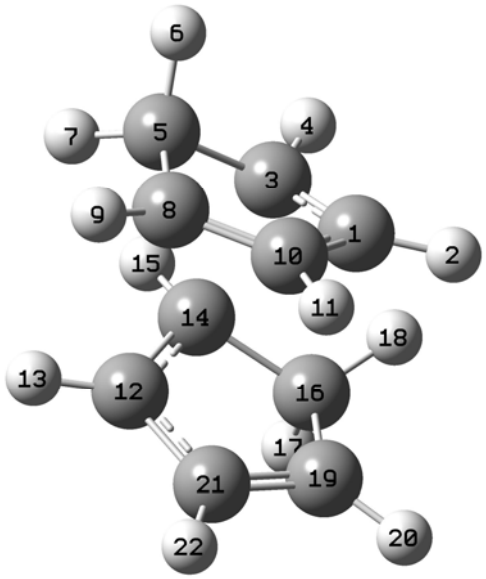

Figure 1 - The cyclopentadiene dimerization transition state. Atom numbers match those in the tables.

Table 3. Angle Parameters

Atom #s	Angle Type	Equilibrium Angle (nm)	Force Constant (kJ mol^{-1} rad^{-2})
3-1-2	C-C-H	118.5	292.88
3-1-10	C-C-C	124	585.76
19-1-10	C-C-C	97.2	260.00
19-1-2	C-C-H	84.3	254.40
19-1-3	C-C-C	91.8	260.00
1-3-4	C-C-H	114.8	292.88
1-3-5	C-C-C	117.6	585.76
4-3-5	H-C-C	113.9	303.34
4-3-14	H-C-C	94.6	370.00
14-3-1	C-C-C	107.2	310.00

14-3-5	C-C-C	101.2	310.00
3-5-6	C-C-H	110.1	303.34
3-5-7	C-C-H	110.1	303.34
3-5-8	C-C-C	111.8	527.18
9-8-12	H-C-C	92.9	40.70
12-8-5	C-C-C	76.2	260.00
12-8-10	C-C-C	87.3	260.00
8-12-13	C-C-H	84.3	254.40
8-12-14	C-C-C	91.7	260.00
8-12-21	C-C-C	96.9	260.00
3-14-12	C-C-C	107.1	310.00
14-12-13	C-C-H	118.5	292.88
14-12-21	C-C-C	124	585.76
3-14-15	C-C-H	94.6	370.00
3-14-16	C-C-C	101.1	310.00
12-14-15	C-C-H	114.8	292.88
12-14-16	C-C-C	117.6	585.76
14-16-17	C-C-H	110.1	303.34
14-16-18	C-C-H	110.1	303.34
14-16-19	C-C-C	111.8	527.18
15-14-16	H-C-C	113.9	303.34
1-19-16	C-C-C	76.5	260.00
1-19-21	C-C-C	87.5	260.00
20-19-1	H-C-C	92.9	40.70

Table 4. Ryckaert-Belleman Torsion Parameters

Atom #s	Torsion Type	C_o (kJ mol^{-1})	C_1 (kJ mol^{-1})	C_2 (kJ mol^{-1})	C_3 (kJ mol^{-1})	C_4 (kJ mol^{-1})	C_5 (kJ mol^{-1})
2-1-3-5	H-C-C-C	34.24120	-1.15740	-30.96780	-2.11610	0.00000	0.00000
2-1-3-4	H-C-C-H	31.60690	0.92940	-31.29710	-1.23920	0.00000	0.00000
10-1-3-5	C-C-C-C	31.54260	-2.97930	-32.08620	3.52290	0.00000	0.00000
10-1-3-4	C-C-C-H	30.93470	-1.08730	-31.29710	1.44970	0.00000	0.00000
1-3-5-6	C-C-C-H	0.08220	-5.01240	-1.11690	6.04710	0.00000	0.00000
1-3-5-7	C-C-C-H	0.08220	-5.01240	-1.11690	6.04710	0.00000	0.00000
1-3-5-8	C-C-C-C	1.34590	-4.71580	-1.04560	4.41550	0.00000	0.00000
4-3-5-6	H-C-C-H	0.65240	1.95730	0.00000	-2.60970	0.00000	0.00000
4-3-5-7	H-C-C-H	0.65240	1.95730	0.00000	-2.60970	0.00000	0.00000
4-3-5-8	H-C-C-C	-0.29900	-0.89700	0.00000	1.19600	0.00000	0.00000
3-5-8-10	C-C-C-C	0.52719	-6.39734	-1.69452	7.56467	0.00000	0.00000
6-5-8-10	H-C-C-C	-0.77822	-2.33467	0.00000	3.11290	0.00000	0.00000
7-5-8-10	H-C-C-C	-0.77822	-2.33467	0.00000	3.11290	0.00000	0.00000
3-5-8-9	C-C-C-H	0.66525	1.99576	0.00000	-2.66102	0.00000	0.00000

5-8-10-11	C-C-C-H	56.91180	-0.07920	-56.68790	-0.14470	0.00000	0.00000
5-8-10-1	C-C-C-C	56.72720	-0.20370	-56.76440	0.24090	0.00000	0.00000
9-8-10-11	H-C-C-H	56.73160	0.06360	-56.71050	-0.08470	0.00000	0.00000
9-8-10-1	H-C-C-C	56.68570	-0.07440	-56.71050	0.09910	0.00000	0.00000
2-1-10-8	H-C-C-C	21.89090	-1.44300	-22.37190	1.92400	0.00000	0.00000
2-1-10-11	H-C-C-H	22.75980	1.16370	-22.37190	-1.55160	0.00000	0.00000
3-1-10-8	C-C-C-C	35.80750	1.48820	-32.85810	-4.43760	0.00000	0.00000
3-1-10-11	C-C-C-H	21.89090	-1.44300	-22.37190	1.92400	0.00000	0.00000
13-12-14-16	H-C-C-C	38.06700	0.66640	-37.84490	-0.88850	0.00000	0.00000
13-12-14-15	H-C-C-H	38.06700	0.66640	-37.84490	-0.88850	0.00000	0.00000
21-12-14-16	C-C-C-C	38.88150	-0.51830	-37.77090	-0.59230	0.00000	0.00000
21-12-14-15	C-C-C-H	38.11590	0.81300	-37.84490	-1.08390	0.00000	0.00000
12-14-16-17	C-C-C-H	0.32800	-5.77740	-1.43590	6.88530	0.00000	0.00000
12-14-16-18	C-C-C-H	0.32800	-5.77740	-1.43590	6.88530	0.00000	0.00000
12-14-16-19	C-C-C-C	2.73330	-1.86590	0.05420	-0.92170	0.00000	0.00000
15-14-16-17	H-C-C-H	0.65950	1.97850	0.00000	-2.63800	0.00000	0.00000
15-14-16-18	H-C-C-H	0.65950	1.97850	0.00000	-2.63800	0.00000	0.00000
15-14-16-19	H-C-C-C	-0.56370	-1.69110	0.00000	2.25480	0.00000	0.00000
21-19-16-14	C-C-C-C	0.52719	-6.39734	-1.69452	7.56467	0.00000	0.00000
21-19-16-17	C-C-C-H	-0.77822	-2.33467	0.00000	3.11290	0.00000	0.00000
21-19-16-18	C-C-C-H	-0.77822	-2.33467	0.00000	3.11290	0.00000	0.00000
20-19-16-14	H-C-C-C	0.66525	1.99576	0.00000	-2.66102	0.00000	0.00000
16-19-21-22	C-C-C-H	50.02890	0.27770	-49.93630	-0.37030	0.00000	0.00000
16-19-21-12	C-C-C-C	50.36830	-0.21600	-49.90540	-0.24680	0.00000	0.00000
20-19-21-22	H-C-C-H	50.02890	0.27770	-49.93630	-0.37030	0.00000	0.00000
20-19-21-12	H-C-C-C	50.02890	0.27770	-49.93630	-0.37030	0.00000	0.00000
13-12-21-19	H-C-C-C	35.32680	1.51970	-32.31520	-4.53130	0.00000	0.00000
13-12-21-22	H-C-C-H	35.32680	1.51970	-32.31520	-4.53130	0.00000	0.00000
14-12-21-19	C-C-C-C	35.32680	1.51970	-32.31520	-4.53130	0.00000	0.00000
14-12-21-22	C-C-C-H	35.32680	1.51970	-32.31520	-4.53130	0.00000	0.00000

Tables 5-8. Isoprene Dimerization (Fig. 2)

Table 5. Charges and Lennard-Jones Parameters

Atom #	Atom Type	q (a.u.)	σ(nm)	ε (kJ mol^{-1})
1	C	-0.196	0.353	0.305
2	H	0.098	0.244	0.126
3	H	0.098	0.244	0.126
14	C	-0.188	0.353	0.302
15	H	0.094	0.245	0.126
16	H	0.094	0.245	0.126

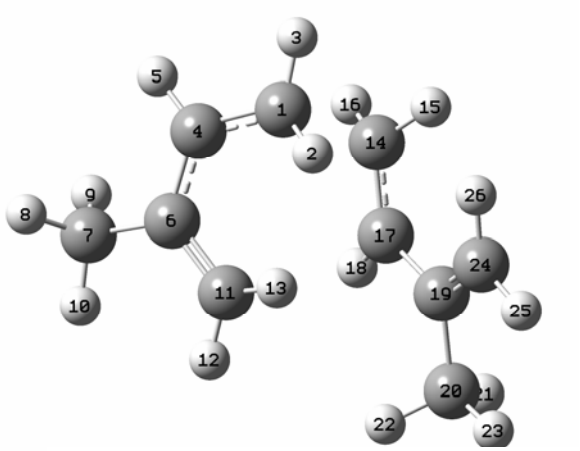

Figure 2 - The isoprene dimerization TS. Atom numbers match those in the tables.

Table 6. Bond Parameters

Atom #s	Bond Type	Equilibrium Length (nm)	Force Constant (kJ mol^{-1} nm^{-2})
1-17	C-C	0.26798	1200
1-4	C-C	0.13987	388800
4-6	C-C	0.14164	363213
6-7	C-C	0.15169	246768
6-11	C-C	0.13748	426234
14-17	C-C	0.14022	383601
17-19	C-C	0.14599	307256
19-20	C-C	0.15141	249441
19-24	C-C	0.13509	467272

Table 7. Angle Parameters

Atom #s	Angle Type	Equilibrium Angle (nm)	Force Constant (kJ mol^{-1} rad^{-2})
2-1-3	H-C-H	114.2	287.74
2-1-4	H-C-C	116.8	292.88
2-1-14	H-C-C	92.7	234.00
3-1-4	H-C-C	116.8	292.88
3-1-14	H-C-C	102.4	234.00
4-1-14	C-C-C	107.3	901.00
1-4-5	C-C-H	119.1	292.88
1-4-6	C-C-C	124.0	585.76
6-11-17	C-C-C	99.3	825.00
17-11-12	C-C-H	111.7	396.00
17-11-13	C-C-H	68.8	396.00
1-14-15	C-C-H	93.4	405.00

1-14-16	C-C-H	99.6	405.00
1-14-17	C-C-C	112.4	901.00
15-14-17	H-C-C	116.5	300.84
16-14-17	H-C-C	116.5	300.84
14-17-18	C-C-H	116.5	300.84
11-17-14	C-C-C	101.0	825.00
11-17-18	C-C-H	80.2	260.00
11-17-19	C-C-C	95.1	194.00
14-17-19	C-C-C	119.1	563.47

Table 8. Ryckaert-Belleman Torsion Parameters

Atom #s	Torsion Type	C_o (kJ mol^{-1})	C_1 (kJ mol^{-1})	C_2 (kJ mol^{-1})	C_3 (kJ mol^{-1})	C_4 (kJ mol^{-1})	C_5 (kJ mol^{-1})
4-6-7-8	C-C-C-H	0.62760	1.88280	0.00000	-2.51040	0.00000	0.00000
4-6-7-9	C-C-C-H	0.62760	1.88280	0.00000	-2.51040	0.00000	0.00000
4-6-7-10	C-C-C-H	0.62760	1.88280	0.00000	-2.51040	0.00000	0.00000
8-7-6-11	H-C-C-C	-0.77822	-2.33467	0.00000	3.11290	0.00000	0.00000
9-7-6-11	H-C-C-C	-0.77822	-2.33467	0.00000	3.11290	0.00000	0.00000
10-7-6-11	H-C-C-C	-0.77822	-2.33467	0.00000	3.11290	0.00000	0.00000
17-19-24-25	C-C-C-H	58.57600	0.00000	-58.57600	0.00000	0.00000	0.00000
17-19-24-26	C-C-C-H	58.57600	0.00000	-58.57600	0.00000	0.00000	0.00000
17-19-20-21	C-C-C-H	0.62760	1.88280	0.00000	-2.51040	0.00000	0.00000
17-19-20-22	C-C-C-H	0.62760	1.88280	0.00000	-2.51040	0.00000	0.00000
17-19-20-23	C-C-C-H	0.62760	1.88280	0.00000	-2.51040	0.00000	0.00000
21-20-19-24	H-C-C-C	-0.77822	-2.33467	0.00000	3.11290	0.00000	0.00000
22-20-19-24	H-C-C-C	-0.77822	-2.33467	0.00000	3.11290	0.00000	0.00000
23-20-19-24	H-C-C-C	-0.77822	-2.33467	0.00000	3.11290	0.00000	0.00000
14-17-19-20	C-C-C-C	-0.77822	-2.33467	0.00000	3.11290	0.00000	0.00000
14-17-19-24	C-C-C-C	21.73797	2.40789	-16.96612	-7.17975	0.00000	0.00000
2-1-4-5	H-C-C-H	41.07150	0.60330	-40.87050	-0.80430	0.00000	0.00000
3-1-4-5	H-C-C-H	41.07150	0.60330	-40.87050	-0.80430	0.00000	0.00000
2-1-4-6	H-C-C-C	40.63520	-0.70570	-40.87050	0.94090	0.00000	0.00000
3-1-4-6	H-C-C-C	40.63520	-0.70570	-40.87050	0.94090	0.00000	0.00000
1-4-6-7	C-C-C-C	29.16980	-1.15670	-29.55530	1.54220	0.00000	0.00000
1-4-6-11	C-C-C-C	40.32510	1.19300	-37.96100	-3.55710	0.00000	0.00000
5-4-6 -7	H-C-C-C	29.86630	0.93280	-29.55530	-1.24370	0.00000	0.00000
5-4-6-11	H-C-C-C	29.16980	-1.15670	-29.55530	1.54220	0.00000	0.00000
4-6-11-12	C-C-C-H	49.17840	-0.36970	-49.30160	0.49290	0.00000	0.00000
4-6-11-13	C-C-C-H	49.17840	-0.36970	-49.30160	0.49290	0.00000	0.00000
7-6-11-12	C-C-C-H	49.40100	0.29810	-49.30160	-0.39750	0.00000	0.00000
7-6-11-13	C-C-C-H	49.40100	0.29810	-49.30160	-0.39750	0.00000	0.00000
15-14-17-18	H-C-C-H	43.13720	0.50160	-42.97000	-0.66880	0.00000	0.00000

16-14-17-18	H-C-C-H	43.13720	0.50160	-42.97000	-0.66880	0.00000	0.00000
15-14-17-19	H-C-C-C	43.17400	0.61200	-42.97000	-0.81600	0.00000	0.00000
16-14-17-19	H-C-C-C	43.17400	0.61200	-42.97000	-0.81600	0.00000	0.00000

Tables 9-11. Hydrogen Transfer between Methane and a Methyl Radical (Fig. 3)

Table 9. Charges and Lennard-Jones Parameters

Atom #	Atom Type	q (a.u.)	σ (nm)	ε (kJ mol^{-1})
1	C	-0.243	0.352	0.292
2	H	0.081	0.245	0.126
3	H	0.000	0.260	0.126
4	H	0.081	0.245	0.126
5	H	0.081	0.245	0.126
6	C	-0.243	0.352	0.292
7	H	0.081	0.245	0.126
8	H	0.081	0.245	0.126
9	H	0.081	0.245	0.126

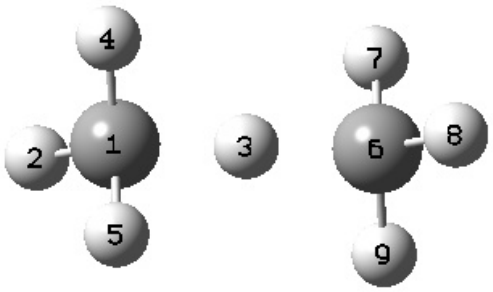

Figure 3 - The methyl-methane hydrogen transfer TS. Atom numbers match those in the tables.

Table 10. Bond Parameters

Atom #s	Bond Type	Equilibrium Length (nm)	Force Constant (kJ mol^{-1} nm^{-2})
1-3	C-H	0.134662	35237
3-6	C-H	0.134662	35237

Table 11. Angle Parameters

Atom #s	Angle Type	Equilibrium Angle (nm)	Force Constant (kJ mol^{-1} rad^{-2})
2-1-4	H-C-H	113.4	282.47
2-1-5	H-C-H	113.4	282.47
4-1-5	H-C-H	113.4	282.47
7-6-8	H-C-H	113.4	282.47
7-6-9	H-C-H	113.4	282.47
8-6-9	H-C-H	113.4	282.47
2-1-3	H-C-H	105.2	214.70
4-1-3	H-C-H	105.2	214.70
5-1-3	H-C-H	105.2	214.70
7-6-3	H-C-H	105.2	214.70
8-6-3	H-C-H	105.2	214.70
9-6-3	H-C-H	105.2	214.70
1-3-6	C-H-C	180.0	91.90

Dihedrals are not included for this system as the torsion energy between the two methyl units was found to be negligible.