Supporting Information for

Lifetimes of Carbocations Encountered along Reaction Coordinates for Terpene Formation

Ryan P. Pemberton and Dean J. Tantillo*

Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, CA 95616, USA

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Section 1. Table showing electronic (both ZPE corrected and uncorrected) and free energies, number of imaginary frequencies (NI), the imaginary frequency for transition states, and relative free energies.

Structure	E (au, no ZPE)	E (au,ZPE)	G (au)	NI	Imag. Freq. (cm-1)	Rel G (kcal/mol)	Comments
1	-390.95553	-390.709148	-390.745623	0		0.0	Rel to **1**
2	-390.95848	-390.709293	-390.743479	0		1.3	Rel to **1**
3	-390.9757	-390.725984	-390.760223	0		-9.2	Rel to **1**
4	-586.2963634	-585.926567	-585.968239	0		0.0	Rel to **4**
5	-586.30134	-585.930508	-585.971672	0		-2.2	Rel to **4**
6	-586.3205495	-585.948892	-585.989893	0		-13.6	Rel to **4**
7	-586.277	-585.911887	-585.958609	0		0.0	Rel to **7**
8	-586.30159	-585.930143	-585.969819	0		-7.0	Rel to **7**
9	-586.31028	-585.937835	-585.977687	0		-12.0	Rel to **7**
10	-430.26636	-429.992224	-430.031145	0		0.0	Rel to **10**
11	-430.27181	-429.994789	-430.031925	0		-0.5	Rel to **10**
12	-430.28912	-430.012082	-430.047627	0		-10.3	Rel to **10**
TS1	-390.94394	-390.695826	-390.729289	1	-294.1793	10.2	Rel to **1**
TS2	-586.28813	-585.917578	-585.957609	1	-264.3012	8.8	Rel to **4**
TS3	-586.29133	-585.921085	-585.959919	1	-218.8105	-0.8	Rel to **7**
TS4	-390.94963	-390.70292	-390.737812	1	-67.6352	4.9	Rel to **1**
TS5	-586.2962943	-585.927167	-585.968415	1	-67.452	-0.1	Rel to **4**
TS7	-430.26682	-429.989227	-430.024098	1	-230.4152		
TS8	-430.2632	-429.98892	-430.026108	1	-42.8437	3.2	Rel to **10**

Section 2. Geometries are included as a separate file attached in *Tripos MOL2* format.

Section 3. Trajectories have been included as separate MPEG-4 (mp4) files for various transformations. The naming of these files begins with the starting transition state (for trajectories including the ammonia theozyme, NH3 and the frozen C-N distance have been added, i.e., NH3_275 mean the ammonia was frozen at 2.75 Å). The end of the name shows the starting and ending points of the trajectory (which were based on the stopping criteria identified in the manuscript).

Section 4.

Full citation for *Gaussian09*:

Gaussian 09, Revision B.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.;

Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Full citation for *Spartan10*:

Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A.Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. Krylov, P.M.W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, **2006**, *8*, 3172-3191.