Direct Dynamics Quasiclassical Trajectory Study of the Stereochemistry of the Vinylcyclopropane−Cyclopentene Rearrangement

Charles Doubleday,*,† Maja Nendel,‡ K. N. Houk,‡ David Thweatt,§ and Michael Page§

*Department of Chemistry, Columbia University
New York, New York 10027
Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90095-1569
Department of Chemistry, North Dakota State University
Fargo, North Dakota 58105*

We report a calculation of the stereochemical product distribution of the vinylcyclopropane (VCP) rearrangement to cyclopentene (CP), based on quasiclassical trajectories run on a modified AM1[1] potential energy surface (PES) parametrized to fit ab initio calculations. This [1,3] sigmatropic shift is an important testing ground for the degree of stereochemical control exerted by the Woodward−Hoffmann rules and for the existence of intermediates in thermal isomerizations. With most substituents[2,3] there is a mild (in some cases, strong[2bc]) preference for W−H allowed reaction. From pyrolyses of the parent *Z*- and *E*-VCP-d_3 at 573 K (Scheme 1 upper left), Baldwin and Anet[4] measured *si:sr:ar:ai* =

Scheme 1
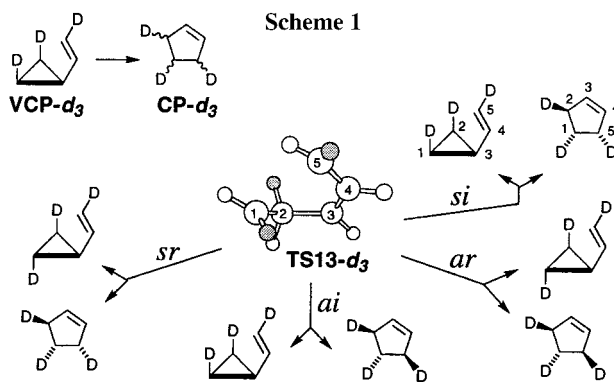
40:23:13:24, where *s,a* refers to suprafacial or antarafacial allylic participation and *r,i* refers to retention or inversion of the migrating methylene. The ratio of allowed (*si* + *ar*) to forbidden (*sr* + *ai*) products is ∼1:1, consistent with a biradical intermediate or with a set of competing direct reactions.

Recently Houk, Nendel, Wiest, and Storer (HNWS)[5] and Davidson and Gajewski (DG)[6] examined this reaction with complementary electronic structure methods. HNWS used DFT with 4-electron−4-orbital complete active space SCF (4,4-CAS) energy corrections, 4,4-CAS/6-31G*//(U)B3LYP/6-31G*, and DG optimized stationary points with 4,4-CAS/6-31G*. The calcula-
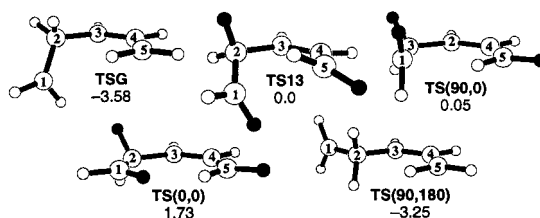

Figure 1. Saddle points used in AM1-SRP fit, reported by HNWS[5] and DG.[6] TS(0,0), TS(90,0), and TS(90,180) have C_s symmetry; (*n,m*) denotes torsion angles about C_1−C_2 and C_2−C_3, respectively. AM1-SRP energies are from Table 1. Shaded H atoms mark D positions used in trajectories.

tions agree on several points. They find no local minimum in the biradical region of the PES. Instead, there is a broad, flat region where all four paths are within 2−3 kcal/mol of each other. The lowest energy saddle point for a 1,3-shift connecting VCP with CP is TS13 (Figure 1), whose intrinsic reaction coordinate (IRC) leads to *si*. To account for the other three paths, HNWS and DG point out that the PES is flat enough to allow two or more paths to merge at TS(90,0) and TS(0,0). Qualitatively, this accounts for all four reactions. However, if a single transition state (TS) mediates two or more reaction paths, then transition-state theory (TST) as currently applied[7] cannot predict a unique product ratio without additional dynamical assumptions.[8] For this reason we have resorted to quasiclassical trajectories, in which the product ratio is given simply by a trajectory count. Recent trajectory studies of trimethylene,[9,10] and prior trajectory studies of 1,3-shifts and other reactions by Carpenter,[8,11] have yielded a better appreciation of the role of dynamics in stereoselection.

To improve the ab initio accuracy by inclusion of dynamical electron correlation, energies were computed by multireference configuration interaction (MRCI) with single and double excitations (excluding the lowest five and highest five MOs) from a 4,4-CAS reference at geometries optimized by 4,4-CAS/6-31G* and 4,4-CAS/cc-pVDZ. Table 1 lists relative MRCI energies corrected by zero-point energy (ZPE) computed from 4,4-CAS analytical second derivatives.

The ab initio PES is fitted by AM1 with specific reaction parameters (AM1-SRP), including 12 AM1 parameters for C and 5 for H. Resonance integrals, core−core repulsions, and electron−nuclear attraction terms are multiplied by constant scaling factors χ_{ij} for C_1C_2, C_2C_3, C_3C_4, C_4C_5, and a single χ value for all C−H pairs. Resonance integrals for C_1C_3 and C_1C_5 are multiplied by distance-dependent factors consisting of tanh functions that switch smoothly between values of χ_{ij} appropriate for large and small distance. Analytical terms are added to correct the otherwise small allylic internal rotation barriers. AM1-SRP parameters are determined by a nonlinear least-squares fit of relative energies and geometries of structures in Figure 1, and energies of VCP and CP, to ab initio data and experimental $\Delta H^{\ddagger}$. All saddle points reported by HNWS and DG are present in AM1-SRP (Table 1).[12] Geometries are close to ab initio geometries, frequencies are reasonably close, transition vectors are similar, and the TS13 IRC is similar to that reported by HNWS.

† Columbia.
‡ UCLA.
§ NDSU.
(1) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985,** *107,* 3902.
(2) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1980; pp 81−87. (b) Gajewski, J. J.; Olson, L. P. *J. Am. Chem. Soc.* **1991,** *113,* 7432−3. (c) Gajewski, J. J.; Olson, L. P.; Willcott, M. R., III. *J. Am. Chem. Soc.* **1996,** *118,* 299−306.
(3) (a) Baldwin, J. E. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: London, 1995; Vol. 2, pp 469−493. (b) Baldwin, J. E. *J. Comput. Chem.* **1998,** *19,* 222−231.
(4) Baldwin, J. E.; Villarica, K. A.; Freedberg, D. I.; Anet, F. A. L. *J. Am. Chem. Soc.* **1994,** *116,* 10845.
(5) Houk, K. N.; Nendel, M.; Wiest, O.; Storer, J. W. *J. Am. Chem. Soc.* **1997,** *119,* 10545−6.
(6) Davidson, E. R.; Gajewski, J. J. *J. Am. Chem. Soc.* **1997,** *119,* 10543.

(7) (a) Truhlar, D. G.; Garrett, B. C.; Klippenstein, S. J. *J. Phys. Chem.* **1996,** *100,* 12771−12800. (b) Hase, W. L. *Acc. Chem. Res.* **1998,** *31,* 659; *Ibid.* **1983,** *16,* 258. (c) Truhlar, D. G.; Isaacson, A. D.; Garrett, B. C. In *Theory of Chemical Reaction Dynamics;* Baer, M., Ed.; CRC Press: Boca Raton, 1985; Vol. IV, p. 65.
(8) Peterson, T. H.; Carpenter, B. K. *J. Am. Chem. Soc.* **1992,** *114,* 766.
(9) (a) Doubleday, C.; Bolton, K.; Hase, W. L. *J. Am. Chem. Soc.* **1997,** *119,* 5251−2. (b) Bolton, K.; Hase, W. L.; Doubleday, C. *Ber. Bunsen-Ges. Phys. Chem.* **1997,** *101,* 414−422. (c) Doubleday, C.; Bolton, K.; Hase, W. L. *J. Phys. Chem. A* **1998,** *102,* 3648−58.
(10) Hrovat, D. A.; Fang, S.; Borden, W. T.; Carpenter, B. K. *J. Am. Chem. Soc.* **1997,** *119,* 5253−4.
(11) (a) Carpenter, B. K. *Acc. Chem. Res.* **1992,** *25,* 520. (b) Carpenter, B. K. *J. Am. Chem. Soc.* **1995,** *117,* 6336. (c) Carpenter, B. K. *J. Am. Chem. Soc.* **1996,** *118,* 10329.

Table 1. Energies Relative to TS13 as the Zero of Energy, Corrected by ZPE (kcal/mol)

	AM1-SRP	HNWS[a]	CAS/1[b]	CAS/2[c]	MRCI/1[d]	MRCI/2[e]
TS(90,0)	0.05	−0.05	−0.18	−0.33	0.86	1.44
TS(90,180)	−3.25	−3.24	−3.22	−3.36	−1.83	−1.01
TSG	−3.58		−3.53	−3.96	−2.13	−2.19
TS(0,0)	1.73	1.07				
VCP-g[f]	−50.67	−45.7	−41.82	−39.56	−46.85	−45.04
VCP-t[f]	−50.37	−46.9[h]	−40.86	−39.38	−47.96	−44.79
CP[g]	−71.94	−66.0[h]	−63.11	−62.63	−69.66	−68.86

a Reference 5, 4,4-CAS/6-31G*//(U)B3LYP/6-31G*, ZPE from (U)B3LYP/6-31G*. *b* 4,4-CAS/6-31G*. *c* 4,4-CAS/cc-pVDZ. *d* MRCI/6-31G*//4,4-CAS/6-31G*, ZPE from 4,4-CAS/6-31G*. *e* MRCI/cc-pVDZ//4,4-CAS/cc-pVDZ, ZPE from 4,4-CAS/cc-pVDZ. *f* Expt: $\Delta H^{\ddagger} = E_a - RT = 50.6$ kcal/mol, gauche (g) + trans (t). Lewis, D. K.; Charney, D. J.; Kalra, B. L.; Plate, A.-M.; Woodard, M. H.; Cianciosi, S. J.; Baldwin, J. E. *J. Phys. Chem. A* **1997**, *101*, 4097. *g* Expt: $\Delta H^{\ddagger} = 72.1$ kcal/mol, ref *f*. *h* B3LYP/6-31G*.

Table 2. Percent Yields from Trajectories Initialized at Three Saddle Points

	TS13[a]	TS(90,0)[b]	TS(0,0)[c]	av[d]	expt4
si	51	27	33	45 ± 4	40
sr	31	20	12	28 ± 3	23
ar	9	19	29	12 ± 3	13
ai	9	34	26	16 ± 3	24
rel part. fcn[e]	1.0	1.5	0.30		
rel weight[f]	0.73	0.23	0.04		

a 373 of 433 trajectories give 1,3-shift. *b* 138 of 755 traj. give 1,3-shift. *c* 58 of 394 traj. give 1,3-shift. *d* ±2 SD. *e* Partition function relative to TS13: AM1-SRP energies, harmonic vibrations excluding torsions, classical rotation. *f* Relative weight in av = (rel part. fcn) × (fraction of trajectories giving 1,3-shift).

Trajectories were initialized at TS13, TS(90,0), and TS(0,0) with quasiclassical TS sampling of a 573 K Boltzmann distribution of normal mode quantum vibrational levels and classical rotational angular momenta.[9c,13] To compute the trajectories we incorporated AM1-SRP into a parallel version of the dynamics program VENUS-MOPAC.[14,15] Each trajectory was run forward and backward in time from its initial point until a product was reached in each direction. The VCP-d_3 and CP-d_3 patterns at these trajectory termini were used to determine the reaction stereochemistry. As an example, Scheme 1 shows four VCP−CP pairs linked by *si*, *sr*, *ar*, *ai* trajectories initiated at TS13-d_3 (D atoms shaded).[16] The *si*:*sr*:*ar*:*ai* ratio is given by the ratio of trajectory counts for each process (Table 2).

Conventional TST predicts only that the relative rate of passage through TS13, TS(90,0), and TS(0,0) is 1.0:1.5:0.3 (Table 2). A TST prediction of stereochemistry would require an assumption about the dynamical accessibility of *si*, *sr*, *ar*, *ai* via each TS.[8]

According to Table 2, the TS region of the PES is shared by all four reactions, as suggested by HNWS[5] and DG[6]—essentially Doering's[17] "continuous diradical as transition state". Baldwin[3b] has recently proposed a model for the VCP rearrangement in which substantial stereochemical scrambling occurs (without an intermediate) in regions of the PES displaced from the TS. Our calculations support this description.

$S(t)$, the fraction of trajectories not cyclized at time t, decays exponentially after an initial 100−200 fs in which no decay

occurs. For 1,3-shift trajectories starting at TS13, TS(90,0), TS-(0,0), the time constant for decay of $S(t)$ is 190, 250, 320 fs, respectively, and the time for $S(t)$ to decay to $1/e$ (including the initial 100−200 fs) is 300, 400, 520 fs. Although exponential decay is consistent with statistical dynamics, we found that fixed energy trajectories display mode selectivity. Four sets of 100 trajectories with zero angular momentum were initialized at TS13 by TS normal mode sampling at fixed energies $E = 3.16$ and 9.82 kcal/mol above the ZPE. At $E = 3.16$, with all vibrational modes in their zero-point level and 3.16 kcal/mol of kinetic energy in the IRC, *si*:*sr*:*ar*:*ai*= 71:8:12:8. At $E = 3.16$ with 3 quanta (2.02 kcal/mol) placed in mode 2 (torsion about C_1-C_2), all other modes in the zero-point level, and 1.14 kcal/mol (*RT*) in the IRC, *si*:*sr*:*ar*:*ai*= 38:39:11:11. At $E = 9.82$ the effect is similar: with all 9.82 kcal/mol in the IRC *si*:*sr*:*ar*:*ai*= 75:4:12:9; with 7.8 kcal/mol in the IRC and 3 quanta in mode 2, *si*:*sr*:*ar*:*ai* = 40:24:8:27. Similar mode selectivity and other nonstatistical effects were reported for trimethylene.[9ab,10]

Mode selectivity implies that intramolecular vibrational redistribution (IVR) is not globally complete on the short time scale of the trajectories. Like trimethylene,[9,10] the trajectories cyclize whenever the termini approach with the right orientation, a process that evidently competes well with IVR. The differences among the columns in Table 2 suggest further that a biradical intermediate with statistical dynamics is not involved. If the reaction did proceed via such an intermediate, then trajectories starting at the 3 TSs would be expected to give the same product ratio, as a result of fast IVR to form a common intermediate.

Trajectories initialized at TS13 give a time-dependent (*si* + *sr*)/(*ai* + *ar*) ratio *R*, equal to 130, 12, and 4.6 at 200, 400, and >600 fs, respectively. This is a manifestation of nonstatistical dynamics and arises from the fact that *s* and *a* trajectories reach TS13 by different routes. Nearly all *s* reaction (98%) occurs by a least-motion rotation of the vinyl group of VCP (torsion about C_2-C_3) toward the plane of the other carbons to make CP. However, 88% of the *a* reaction occurs by rotating the long way around through an anti conformation (e.g., TS(90,180)). As a result, *a* trajectories travel a much greater distance from VCP to CP than *s* trajectories. High cyclization efficiency implies that *R* is kinetically determined by the relative times of travel along the *s* and *a* paths and that *R* should be time-dependent. For trajectories initialized at TS(90,0), the routes taken by *s* and *a* trajectories are similar, and *R* is not time-dependent.

To examine the degree to which each torsion is correlated with its previous motion, we computed the rms cumulative torsional displacement $\Delta_{ij}(t) = \langle[\theta_{ij}(t) - \theta_{ij}(0)]^2\rangle^{1/2}$, where $\theta_{ij}(t)$ is the cumulative torsion angle about the C_i-C_j bond (C_1-C_2 or C_2-C_3) at time t and $\langle...\rangle$ denotes an ensemble average. Correlated motion that approximately conserves torsional angular momentum[8,11] would be expected of a direct mechanism and would give a linear t-dependence of $\Delta_{ij}(t)$. For trajectories initialized at TS13, $\Delta_{12}(t)$ increases linearly in t over 50−600 fs with an angular velocity $\Omega = 10^{13}$ radians/s. $\Delta_{23}(t)$ is linear up to 400 fs (75% decay of $S(t)$) with $\Omega = 0.7 \times 10^{13}$ radians/s, but for t > 400 fs $\Delta_{23}(t)$ is essentially stationary. This signals a qualitative change in the C_2-C_3 torsional dynamics at long times. Trajectories initialized at TS(90,0) give a linear t-dependence of $\Delta_{12}(t)$ and $\Delta_{23}(t)$ over 100−700 fs. In summary, ∼80% of the VCP rearrangement consists of four sets of competing direct reactions. The remainder involves more complex C_2-C_3 torsional motion.

Supporting Information Available: AM1-SRP specification and geometries of stationary points, MRCI total energies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(12) A very shallow minimum lies 1.2 kcal/mol below TS(90,180), with a structure that deviates from (0,180) by a 5° conrotatory double rotation. The ZPE-corrected barrier to conrotatory cyclization is 0.1 kcal/mol.

(13) Here, trajectories were initialized only with the d_3 patterns shown in Figure 1. A complete treatment is planned, including all relevant d_3 patterns.

(14) Peslherbe, G. H.; Bolton, K.; Doubleday, C.; Hase, W. L. VENUS-MOPAC, a General Chemical Dynamics and Semiempirical Direct Dynamics Computer Program. To be released.

(15) Stewart, J. J. P. "MOPAC 7.0, a General Molecular Orbital Package" QCPE455.

(16) In Scheme 1 the vinyl group of VCP is cis to C_2-D. A set of products is also formed in which they are trans. The uniqueness of each atom guarantees an unambiguous assignment of *si*, *sr*, *ar*, or *ai*.

(17) Doering, W. von E.; Sachdev, K. *J. Am. Chem. Soc.* **1974**, *96*, 1168.