J|A|C|S
COMMUNICATIONS

Ab Initio Direct Dynamics Study of Cyclopropyl Radical Ring-Opening

David J. Mann and William L. Hase*

Department of Chemistry and Institute for Scientific Computing, Wayne State University, Detroit, Michigan 48202

Received October 22, 2001

The stereochemistry of the electrocyclic ring-opening reaction of the cyclopropyl radical has been a long-standing question.[1] For other pericyclic reactions, such as the ring-opening of cyclopropane and cyclobutene, the Woodward−Hoffmann rules predict conrotatory and disrotatory stereochemistry, respectively.[2] Unfortunately, for the case of the cyclopropyl radical, the Woodward−Hoffmann rules predict both conrotatory and disrotatory modes as nominally forbidden.[3] In early experimental work by Thynne,[4] cyclopropyl radicals were generated by the methyl-radical-induced decomposition of cyclopropane−carboxaldehyde. At 174 °C they found that 10% of the cyclopropyl radicals formed react by ring-fission to form allyl radicals. With the absence of any experimental data on the cyclopropyl radical ring-fission mechanism, predictions of its preferred stereochemistry have relied on theoretical calculations.

The earliest semiemperical calculations predicted a conrotatory ring-opening mechanism, with synchronous rotation of the terminal methylene groups.[1] Higher-level UHF/3-21G and CASSCF/3-21G calculations by Olivella et al.[3] identified a highly asynchronous transition structure with C_1 symmetry (see Figure 1). In a recent theoretical study at the B3LYP/6-311G(2d) level,[5] intrinsic reaction coordinate (IRC) calculations were carried out from the C_1 transition state (TS) to the allyl radical, and the overall reaction was found to occur with disrotatory stereochemistry. On the basis of surface topology, the asynchronous structure of the two methylene groups at the TS would favor a nonconcerted ring-opening mechanism, in which one methylene group completes its rotation before the other. This was observed from both Olivella and Carpenters IRC calculations.[3,5] However, it is not clear from the IRC calculations alone that the topologically disrotatory nature of the TS should favor disrotatory stereochemistry under experimental conditions. TS vibrational zero-point energy (zpe) can influence the relative importance of multiple reaction pathways as the reactive system moves off the TS. In addition, mode−mode coupling may affect the reaction mechanism.

In this contribution, we present results from a high-level ab initio direct dynamics quasiclassical trajectory study of the ring-opening of the cyclopropyl radical under experimental conditions,[4] which for the first time directly probe the ring-fission mechanism and dynamics. The direct dynamics[6−9] method has been applied successfully to the study of similar ring-opening reactions. In this method, classical trajectories are computed directly on an ab initio potential energy surface (PES). We begin the trajectories at the C_1 TS and randomly perturb this structure with quasi-classical normal mode sampling[10] at the experimental temperature of 174 °C. Zero-point and thermal vibrational energy are included in the initial conditions. The latter is sampled from the normal mode Boltzmann distribution. In addition, a rotational energy of RT/2 is added to each rotational axis, and a translational energy, randomly sampled from a thermal Boltzmann distribution,[11] is added to the reaction coordinate directed toward the allyl radical product. The algorithms for sampling initial conditions were taken from the chemical dynamics program VENUS[12] and incorporated into a modified version of the GAMESS[13] electronic structure program. Structures for the cyclopropyl and allyl radicals along with the C_1 TS are shown in Figure 1. The allyl product was identified as either cis or trans by the positions of atoms 4 and 7. The cis configuration formed by the disrotatory motion of the IRC is shown in Figure 1. The other cis configuration and the two trans configurations are not shown. The trajectories reported here only probe the dynamics as the reactive system moves from the TS to the allyl radical. Although of importance and of much interest, subsequent intramolecular vibrational energy redistribution (IVR) processes of the radical are not considered.

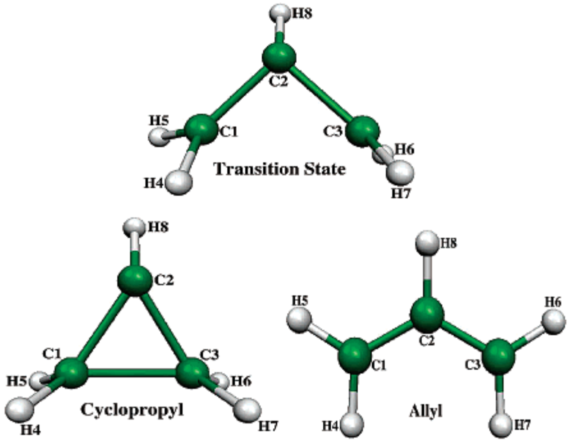

Figure 1. Structures of the cyclopropyl radical, C_1 ring-opening transition state, and the allyl radical (the isomer formed by the disrotatory motion of the IRC).

The trajectories are calculated on the electronically adiabatic ground-state doublet PES at the CASSCF(3,3)/6-31G(d) level of theory,[14] where nonadiabatic electronic surface-crossing is not allowed. The (3,3) active space involves the radical orbital and the σ and σ^* orbitals of the breaking σ bond occupied by the unpaired electron and the two electrons in the breaking σ bond, respectively. These orbitals transform into the three π orbitals of the allyl radical.

The resulting CASSCF(3,3)/6-31G(d) zpe-corrected barrier height of 22.2 kcal/mol agrees with the experimental value[15,16] of 22 ± 2 kcal/mol and a recent CCSD(T)/6-311G(2d) result of 22.5 kcal/mol.[5] The computational expense at this level of theory limits the number and duration of computed trajectories. A single 200 fs trajectory, integrated with a 0.2 fs time-step, takes approximately 5 cpu hours on a single R12K processor.

As a first step in examining the ring-fission mechanism and dynamics, a total of 141 trajectories are integrated for 200 fs each, where formation of the allyl radical typically occurs during the first

---

* To whom correspondence should be addressed. E-mail: wlh@cs.wayne.edu.

10.1021/ja017343x CCC: $22.00

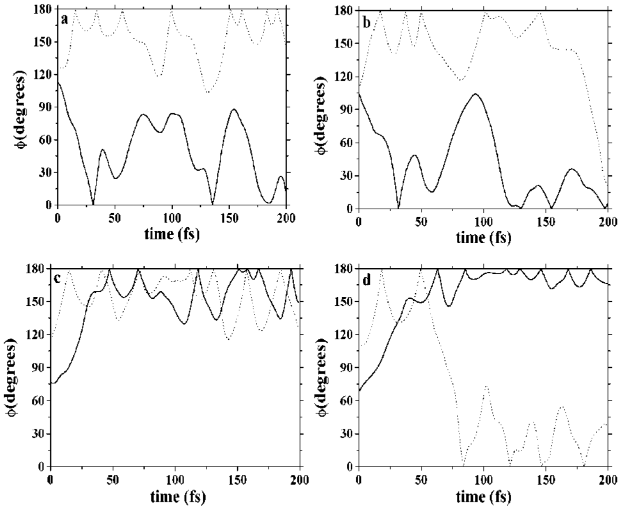

Figure 2. Plots of the ϕ_1 (···) and ϕ_2 (—) torsion angles for the four trajectory types observed in the simulations; (a) con/trans, (b) con/cis, (c) dis/cis, (d) dis/trans. The label dis/trans, for example, represents a trajectory for which the initial rotation of the methylene groups is disrotatory, directed toward the cis isomer in Figure 1, but further methylene rotation after 200 fs of dynamics leads to a trans configuration.

30−60 fs of dynamics. Two key features of the dynamics are investigated: the initial rotation of the two methylene groups, and the final stereochemistry at the termination of each trajectory. This was accomplished by animating each trajectory and analyzing the $H_5-C_1-C_2-C_3$ (ϕ_1) and $H_6-C_3-C_2-C_1$ (ϕ_2) torsion angles versus time.

The trajectories exhibit several unique types of dynamical behavior. Barrier recrossing after 12−21 fs of dynamics is observed from 21 of the 141 trajectories leading to the cyclopropyl radical, a violation of transition-state theory. Additional recrossing of the TS was not observed. Initially, 68 of the 120 reactive trajectories followed the asynchronous disrotatory motion of the IRC, leading to the cis isomer in Figure 1. The $H_5-C_1-H_4$ group first rotated, followed by rotation of the second methylene group. The remaining 52 trajectories also had an asynchronous motion similar to the IRC, except the $H_6-C_3-H_7$ methylene group rotated in the opposite direction, forming the conrotatory, trans isomer with H_7 in Figure 1 pointing up. The preference found here for disrotatory motion agrees with Carpenter's predictions, but a sizable amount (43%) of the trajectories follow the conrotatory path. In all of the reactive trajectories the rotations of the terminal methylene groups are nonconcerted, in agreement with the previous IRC calculations.[3,5] The average time between the initial rotations of the two methylene groups was determined to be 35 fs for the conrotatory trajectories and 56 fs for the disrotatory trajectories.

The initial rotation of the methylene groups may not determine the final cis or trans stereochemistry of the unlabeled allyl radical product. For the 200 fs of dynamics followed here, the trajectories fall into four distinct categories, where each is depicted from the plots of the ϕ_1 and ϕ_2 torsion angles in Figure 2. These are either the direct process described above (Figure 2, a and c), where only an initial rotation of the methylene groups occurs (con/trans and dis/cis), or indirect (Figure 2, b and d), where a subsequent rotation of one of the methylene groups follows formation of the allyl radical (con/cis and dis/trans). The number of trajectories for the four categories identified by Figure 2, a−d are 27, 25, 46, and 22, respectively. For approximately 50% of the reactive trajectories subsequent rotations of one of the methylene groups follow the formation of the allyl radical, altering the product stereochemistry. If the allyl radical is formed with a vibrationally excited CH_2 wagging mode, additional rotations of the methylene group may occur. From approximately 40% of the reactive trajectories subsequent rotations of one of the methylene groups follow the formation of the allyl radical, altering the product stereochemistry. With a CASSCF barrier of 17.2 kcal/mol for internal rotation of the allyl radical and an average energy of 84 kcal/mol above this barrier, the RRKM rate constant for isomerization was determined to be $2.05 \times 10^{12}\ s^{-1}$, corresponding to a lifetime of 488 fs for the allyl radical. The number of cis and trans isomers formed after 200 fs of dynamics was 71 and 49, respectively, only slightly different from the initial amounts. Because of the slow IVR of the excited CH_2 wagging mode and a trajectory integration time shorter than the RRKM internal rotation lifetime, obtaining the statistical cis/trans ratio of 1/1 is not expected.

The initial conditions leading to the disrotatory, conrotatory, and barrier recrossing trajectories were analyzed to determine those conditions, if any, that favor the three observed types of dynamics. The averages of the initial reaction coordinate translational energy are 1.25 kcal/mol for the disrotatory trajectories, 0.64 kcal/mol for the conrotatory trajectories, and 0.23 kcal/mol for those trajectories that recrossed the barrier. This result is surprising and suggests a possible correlation between reaction coordinate translation and reaction stereochemistry. A small ensemble of 10 trajectories, all initiated with a reaction coordinate translational energy of 4 RT (3.55 kcal/mol), resulted in disrotatory stereochemistry.

In summary, the results from the ab initio quasi-classical trajectories provide evidence for both disrotatory and conrotatory ring-opening of the cyclopropyl radical at 174 °C. We find a small (57%) preference for disrotatory ring-opening; however, given the limited number of trajectories performed in this study it is possible that a larger ensemble of trajectories may predict no stereochemical preference for ring-opening. The possible existence of a valley−ridge inflection (VRI) point along the PES, as suggested by Carpenter,[17] may help explain the mixture in stereochemistry observed from these trajectories. Future studies will attempt to address this issue, in addition to the role of reaction coordinate translational energy on the initial reaction stereochemistry.

Acknowledgment. We thank Barry Carpenter for helpful discussions.

References

(1) Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 395.
(2) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim/Deerfield Beach, 1970.
(3) Olivella, S.; Solé, A.; Bofill, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2161.
(4) Greig, G.; Thynne, J. C. C. *Trans. Faraday Soc.* **1967**, *63*, 1369.
(5) Arnold, P. A.; Carpenter, B. K. *Chem. Phys. Lett.* **2000**, *90−96*, 328.
(6) Doubleday, C.; Bolton, K.; Hase, W. L. *J. Am. Chem. Soc.* **1997**, *119*, 22.
(7) Doubleday, C.; Bolton, K.; Hase, W. L. *J. Phys. Chem. A* **1998**, *102*, 3648.
(8) Ben-Nun, M.; Martínez, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 6299.
(9) Doubleday, C. *J. Phys. Chem. A* **2001**, *105*, 6333.
(10) Chapman, S.; Bunker, D. L. *J. Chem. Phys.* **1975**, *62*, 2890. Sloane, C. S.; Hase, W. L. *J. Chem. Phys.* **1977**, *66*, 1523. Hase, W. L.; Ludlow, D. M.; Wolf, R. J.; Schlick, T. *J. Phys. Chem.* **1981**, *85*, 958.
(11) Bunker, D. L. *Methods Comput. Phys.* **1971**, *10*, 287.
(12) Hase, W. L.; Duchovic, R. J.; Hu, X.; Komornicki, A.; Lim, K. F.; Lu, D.-H.; Peslherbe, G. H.; Swamy, K. N.; Vande Linde, S. R.; Varandas, A.; Wang, H.; Wolf, R. J. *QCPE* **1996**, *16*, 671.
(13) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, S. Su; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.
(14) The second-order method for orbital optimization of MCSCF wave functions is used. Chaban, G.; Schmidt, M. W.; Gordon, M. S. *Theor. Chem. Acc.* **1997**, *97*, 88.
(15) Kerr, J. A.; Smith, A.; Trotman-Dickenson, A. F. *J. Chem. Soc. A* **1969**, 1400.
(16) Walsh, R. *Int. J. Chem. Kinet.* **1970**, *2*, 71.
(17) Private communication.

JA017343X