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Bimodal Distribution of Lifetimes for an Intermediate from a Quasiclassical Dynamics Simulation

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Mechanistic analysis of the thermal reactions of polyatomic molecules is generally predicated on the assumption that any reactive intermediates will have lifetimes that can reasonably be described by statistical models of kinetics such as Transition State Theory (TST)[1] or RRKM theory.[2] The quasiclassical dynamics simulations described in the present work suggest that this assumption may not always be justified. They indicate that a thermally generated intermediate can exhibit a distinctly bimodal distribution of lifetimes, with the short-lived population reacting orders of magnitude faster than the statistical kinetic models would predict. It is possible that such nonstatistical behavior may be at the root of some of the "stepwise vs concerted" mechanistic disputes that have plagued mechanistic chemistry in recent years.[3]

The reaction being simulated in the present work is the thermal interconversion of bicyclo[3.2.0]hept-2-ene, **1**, and bicyclo[2.2.1]hept-2-ene, **3**, by way of the singlet-state biradical **2**. The potential energy surface[4] for this reaction was computed with both AM1[5] and PM3[6] semiempirical molecular orbital methods,[7] using the minimal configuration interaction necessary for reasonable description of a singlet-state biradical within the molecular orbital framework.[8] As shown in the enthalpy profile in Figure 1, the two models agree that intermediate **2** occurs as a distinct local minimum, but disagree about the depth. This difference in the two models was exploited in order to investigate the dependence of the dynamics on the details of the potential energy surface.[9]

Classical trajectories were run on both surfaces using the direct dynamics procedure.[10] A quasiclassical canonical ensemble (T = 300 °C) of vibrational states was prepared in the vicinity of the transition structure linking **2** and **3**. Rotations of the initial structures were not energized. Each trajectory was allowed to evolve for at least 500 fs. Each of the semiempirical surfaces was explored with 100 trajectories—a sufficiently small number that only qualitative conclusions can be drawn from the results.

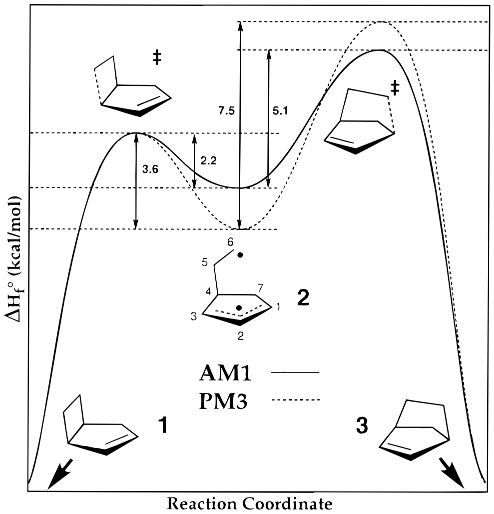

Figure 1. Enthalpy profiles for the interconversion of **1** and **3** via intermediate **2**, computed using semiempirical molecular orbital methods with the AM1 and PM3 hamiltonians.

Within the first 150−250 fs, each of the trajectories approached a geometry that was quite close to the transition structure linking the biradical **2** and compound **1**. Some of them passed through this region and on to the minimum corresponding to compound **1** in a total time of about 250−350 fs. Others failed to take the exit, instead appearing to remain trapped in the region of the biradical for considerably longer.[11] The assumption was made that those trajectories failing to escape from the biradical region on the first attempt would have lifetimes in the local minimum that could reasonably be predicted by RRKM theory.[12] The RRKM calculations[13] used the same energy surface, moments of inertia, and vibrational frequencies that had been employed in the dynamics calculations.

As summarized in Figure 2, four of the trajectories on the PM3 surface were of the type that formed the product in a single pass. On the AM1 surface, 10 of the 100 examined showed this behavior. It seems plausible that the larger proportion of direct trajectories on the AM1 surface is related to the fact that the biradical sits in a shallower potential energy well in that model. Such a relationship could be expected because intermediates in very shallow potential-energy wells generally have

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(1) Pelzer H.; Wigner E. *Z. Phys. Chem.* **1932**, *B15*, 445. Glasstone S.; Laidler K. J.; Eyring H. *Theory of Rate Processes*; McGraw-Hill: New York, NY, 1940.

(2) Rice, O. K.; Ramsperger, H. C. *J. Am. Chem. Soc.* **1927**, *49*, 1617. Rice, O. K.; Ramsperger, H. C. *J. Am. Chem. Soc.* **1928**, *50*, 617. Kassel, L. S. *J. Phys. Chem.* **1928**, *32*, 225. Kassel, L. S. *J. Phys. Chem.* **1928**, *32*, 1065. Marcus, R. A.; Rice, O. K. *J. Phys. Colloid Chem.* **1951**, *55*, 894. Marcus, R. A. *J. Chem. Phys.* **1952**, *20*, 359. Robinson, P. J.; Holbrook, K. A. *Unimolecular Reaction*; Wiley: New York, NY, 1971. Forst, W. *Unimolecular Reactions*; Academic Press: New York, NY, 1973.

(3) See, for example: Lehr, R. E.; Marchand, A. P. In *Pericyclic Reactions*; Marchand, A. P.; Lehr, R. E., Eds.; Academic Press: New York, NY, 1977; Vol. 1.

(4) Since the AM1 and PM3 semiempirical methods are calibrated against experimental heats of formation, they calculate enthalpies rather than potential energies. The surface used for the dynamics was thus strictly an enthalpy surface rather than a potential energy surface, but it is assumed that the error arising from equating relative enthalpy and relative potential energy is small, compared to the overall errors in the semiempirical methods.

(5) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(6) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

(7) Calculations were carried out with Revision 2 of the MOPAC93 package (J. J. P. Stewart, Fujitsu Limited, Tokyo, Japan, 1993).

(8) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(9) It is perhaps useful to emphasize that the point of the present work is to compare the predictions from two different kinetic models on the same potential energy surfaces. Whether the surface itself is accurate for the particular reaction selected is an important question when one comes to compare theory with specific experiments, but not important for the purpose of comparing the kinetic models or addressing general behavior of reactive intermediates.

(10) For an example and key references, see: Liu, Y.-P.; Lu, D.; Gonzalez-Lafont, A.; Truhlar, D. G.; Garrett, B. C. *J. Am. Chem. Soc.* **1993**, *115*, 7806.

(11) Animations of one direct trajectory and one "statistical" trajectory can be viewed by the interested reader on the World Wide Web (http://www.chem. cornell.edu/~bkc1/dynamics.html).

(12) A somewhat similar procedure for mixing exact classical dynamics and statistical approximations can be found in: Hamilton and Brumer (Hamilton, I.; Brumer, P. *J. Chem. Phys.* **1985**, *82*, 1937), although the criterion for distinguishing between "statistical" and "nonstatistical" populations in that work is different from the one used here. It should be noted that the "lifetimes" computed for the two subsets of trajectories in the present work have somewhat different meanings. For the direct trajectories, the lifetimes are defined as the times required for each trajectory to evolve from its starting state to a state in which the carbon atoms whose bonding serves to close the four-membered ring of compound **1** approach each other within the sum of their covalent radii. For the "statistical" set the distribution of lifetimes comes from the reciprocal of the RRKM microcanonical rate constant for each indvidual starting state. Errors in relative lifetime of the two populations that arise from this difference in definition cannot be large enough to recombine the two subsets into a single population.

(13) RRKM calculations were performed with the program by: Hase, W. L.; Bunker, D. L. *QCPE* **1975**, No. 234.

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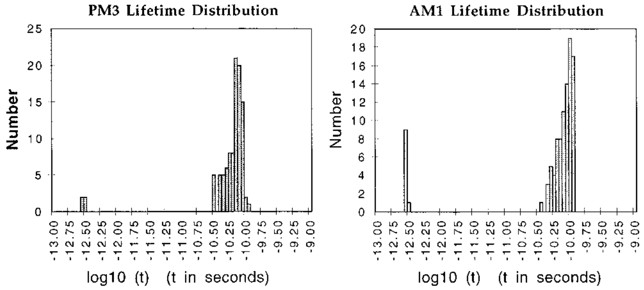

Figure 2. Lifetime distributions for intermediate **2** from quasiclassical trajectory calculations and RRKM calculations on the AM1 and PM3 energy surfaces. See footnote 12 for further information.

"wide" exit channels that are more likely to be traversed by the direct trajectories. Since the best thermochemical estimates[14] indicate that the barrier to closure of the biradical is only 1.3 kcal/mol, smaller even than that suggested by AM1, it also seems likely that the proportion of direct trajectories in the real system would be higher than seen in either simulation.

The two populations of intermediates revealed by this simulation differed not only in their lifetime but also in their likely selection of exit channels. The formation of the new C−C bond in **1** can occur with two possible stereochemistries that are distinguishable by isotopic labeling of the hydrogens,[14,15] but are degenerate for the unsubstituted molecules. These two channels correspond to inversion and retention of configuration at C6. The degeneracy implies that biradicals exhibiting statistical behavior (the longer-lived population) should choose the exit channels with equal probability. By contrast, all of the trajectories corresponding to nonstatistical dynamics (the four on the PM3 surface and ten on the AM1 surface) formed compound **1** with inversion of configuration. The experimental fact is that inversion of configuration is favored in this reaction.[14,15]

An apparent failure of the TST and RRKM statistical approximation is indicated by the existence of the direct trajectories in the present simulation. These intermediates are formed with a distribution of internal energy that is very close to that required for exit from the biradical local minimum. However, this is possible only if the dynamics for entrance to the intermediate region can be strongly coupled to the dynamics for exit.[16] In the present case the inversion exit channel is much more strongly coupled to the entrance than is the retention exit channel, despite the degeneracy that ensures identical geometries and potential energies for the two transition structures leading from biradical **2** to compound **1**. Possible reasons for this have been discussed previously.[16]

Using a statistical kinetic model, the only way to explain the experimental results implied by the present simulation would be to assign two competing mechanisms to the reaction. Given the disparate lifetimes and stereochemical selectivities of the two populations, one might well believe that the direct trajectories corresponded to a "concerted" mechanism, involving no intermediate, while the others corresponded to a "stepwise" mechanism in which an intermediate was involved. However, in the usual language of chemistry, different mechanisms for a reaction imply different potential energy surfaces. The present simulation reveals the existence of two dynamic populations on the same potential energy surface.

The distinction is more than semantic. One can think of influencing the fraction of intermediates belonging to one dynamic population or the other (for example by imposing an isotope effect on the entrance channel, or by changing the collision frequency of the reacting molecule with others in the system) with results that would be hard to explain in the competing-mechanism model. Furthermore, the selection of exit channel by the direct trajectories is a phenomenon of dynamic origin in one model, but must be explicable in terms of static bonding effects[17] in the other.

There is no obvious reason why the particular surfaces explored in the present simulation should be unique; it seems possible that the occurrence of bimodal lifetime distributions could be quite common for reactive intermediates.[18] Mechanistic analyses that assumed statistical kinetic behavior in such cases would generally be incorrect.

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(14) Klärner, F.-G.; Drewes, R.; Hasselman, D. *J. Am. Chem. Soc.* **1988**, *110*, 297.

(15) Berson, J. A.; Nelson, G. L. *J. Am. Chem. Soc.* **1967**, *89*, 5502. Berson, J. A.; Nelson, G. L. *J. Am. Chem. Soc.* **1970**, *92*, 1096. Baldwin, J. E.; Belfield, K. D. *J. Am. Chem. Soc.* **1988**, *110*, 296.

(16) Carpenter, B. K. *J. Am. Chem. Soc.* **1995**, *117*, 6336.

(17) For example: Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, 1970.

(18) The coexistence of statistical and direct trajectories in systems with a small number of atoms has been known for some time. See, for example: Davis, M. J.; Gray, S. K. *J. Chem. Phys.* **1986**, *84*, 5389. Davis, M. J. *J. Chem. Phys.* **1987**, *86*, 3978. Levine has reported similar behavior in the dynamics of electronically excited molecular iodine (Levine, R. D. lecture at the 35th IUPAC Congress on Physical Chemistry, Turkey, 1995). Frequently, the direct trajectories in these systems are *non*reactive, for example: Simonson, M.; Bradley, K. S.; Schatz G. C. *Chem. Phys. Lett.* **1995**, *244*, 19. Pais, A. A. C. C; Voronin, A. I.; Varandas, A. J. C. *J. Phys. Chem.* **1996**, *100*, 7480. To the author's knowledge, the prior work most closely related to the present study is that involving the gas-phase S_N2 reaction: Vande Linde, S. R.; Hase, W. L. *J. Am. Chem. Sco.* **1989**, *111*, 2349. Hase, W. L. *Science*, **1994**, *266*, 998. There appears to have been no prior discussion of the difference in selection of product exit channels by direct and statistical trajectories.