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Nonstatistical Dynamics in Unlikely Places: [1,5] Hydrogen Migration in Chemically Activated Cyclopentadiene

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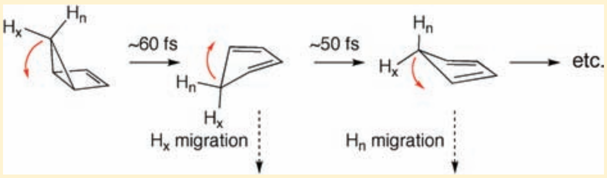
S *Supporting Information*

ABSTRACT: A molecular dynamics simulation reveals the occurrence of nonstatistical dynamical effects in the ring-opening and subsequent [1,5] H migration of bicyclo[2.1.0]pent-2-ene. The symptoms of the effects do not show up in the overall kinetics or product branching ratios of the reaction, which are well explained by a master-equation analysis, but in an oscillatory preference for migration of the two methylene hydrogens. It is predicted that these oscillations could have an observable effect on final product ratios in isotopically labeled analogues, and that the effect might be greater in certain solvents than in the gas phase.



INTRODUCTION

Accumulating evidence from laboratories around the world, studying an ever-widening range of reaction types, points to an important role for nonstatistical dynamical effects in the thermal reactions of polyatomic molecules.[1−18] When such effects occur, the results can be disruptive to the conventional models of reaction mechanisms. For example, reactive intermediates can behave in ways that depend on how they were prepared,[19] they can form products in ratios that are not predictable from the barriers on the standard free energy surface (in extreme cases even favoring the pathway that has the highest barrier[4]), and they can choose exit channels in a manner that shows oscillatory time dependence.[20] As dramatic as these effects may seem, the computational and/or experimental techniques required to differentiate them from more conventional and familiar phenomena are not in common use. Consequently, there is the potential to generate an incorrect mechanism by assuming statistical behavior for a reaction in which nonstatistical dynamical effects are occurring covertly. It is therefore of some importance to understand when more conventional, statistical models of reaction kinetics, such as RRKM theory[21−24] and Transition State Theory[25,26] (TST), are expected to be adequate. However, a general statement of the criteria to be satisfied for the adequacy of statistical models has not yet been forthcoming, despite the intense activity in this field.

The study described in this Article was undertaken with a view to probe the parameters of the problem by studying a reaction for which existing experimental evidence showed interesting and unusual behavior, but for which symmetry arguments suggested that the dynamical couplings previously associated with certain nonstatistical effects[20] ought to be weak, at best. If the detailed dynamical study had shown statistical behavior, then the symmetry criterion might have become a candidate for addition to a list of conditions whose satisfaction would be deemed sufficient to allow confident application of RRKM or TST analyses. However, as described below, that was not the outcome.

The prototype for the reaction sequence of interest is the thermal ring-opening of bicyclo[2.1.0]pent-2-ene (BCP) to 1,3-cyclopentadiene[27] (CP), followed by degenerate [1,5] hydrogen migration in the latter (Figure 1). Following some initial confusion about the facts,[28−31] a careful study on the rearrangement of 2-methylbicyclo[2.1.0]pent-2-ene (2-MeBCP) revealed that both 2-methyl-1,3-cyclopentadiene and 1-methyl-1,3-cyclopentadiene (2-MeCP and 1-MeCP, respectively) were formed, and that the amount of the latter was greater than would be expected on the basis of thermally activated isomerization of 2-MeCP at the reaction temperature (see Scheme 1).[32] This was found to be true in both gas-phase and solution-phase reactions. A number of hypotheses were advanced for the observation, but in the end the generally agreed explanation is now that the initially formed 2-methylcyclopentadiene is chemically activated (2-MeCp*), and that its rearrangement can occur in competition with collisional cooling.[32,33] For this to be true in solution, where effective collision frequencies are thought to be ∼10^{13} s^{-1},[34] the rearrangement must presumably be occurring very rapidly. One might then wonder whether the rearrangement could be taking place on the picosecond time scale believed to be typical for intramolecular vibrational energy redistribution (IVR),[35,36] in which case a fundamental requirement for the validity of statistical kinetic models might be contravened.

The chemical activation of the initially formed cyclopentadiene arises from a combination of the barrier to the initial ring-opening and its overall exothermicity. Values for both of these

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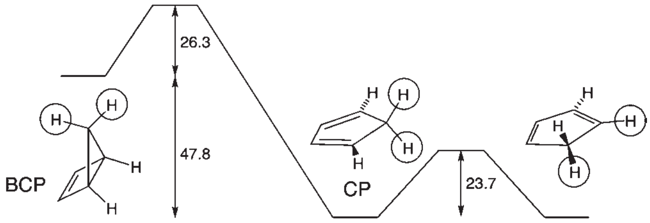
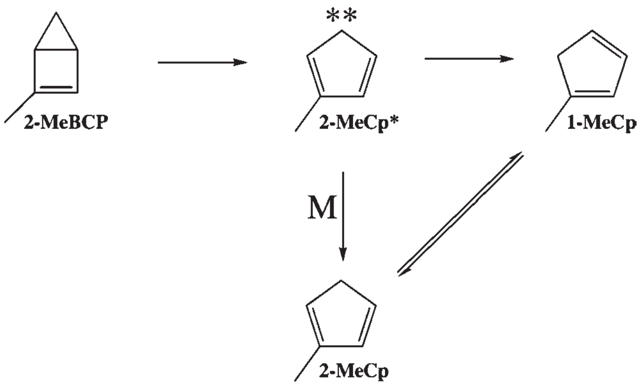


Figure 1. Experimental enthalpy changes in kcal/mol for the ring-opening of bicyclo[2.1.0]pent-2-ene (BCP) and susbsequent [1,5] H migration in cyclopentadiene (CP).

Scheme 1. Mechanism for the Ring-Opening and Subsequent Rearrangement of 2-Methylbicyclo[2.1.0]pent-2-ene[a]



[a] 2-MeCp* is a chemically activated initial product that is cooled by collision with molecules, M, of the bath.

quantities are available from experiment[37,38] for the parent BCP and are shown in Figure 1, along with the barrier to [1,5] hydrogen migration in CP.[39]

In previous attempts to understand nonstatistical dynamical effects, we have focused on the coupling between the dynamics of formation of a reactive intermediate and those for its subsequent reactions. Sometimes a particular product can be favored because the dynamics of its formation are particularly strongly coupled to those of the entrance channel into the preceding reactive intermediate, a phenomenon that we have termed dynamic matching.[40] However, in the present case, coupling of entrance and exit channel dynamics looked from the outset as if it should be weak at best, because the vibrational modes excited by the ring-opening reaction are of different symmetry from most of the modes that need to be energized for the [1,5] hydrogen migration. Specifically, in the C_s point group of the reactant, the ring-opening reaction coordinate has A' symmetry. Hence, the vibrational modes of cylopentadiene that would be excited by its formation from the ring-opening transition state ought to be of A_1 and B_1 symmetry only (the irreducible representations of cyclopentadiene's C_{2v} point group that transform into A' in C_s). By contrast, the methylene C−H bending modes whose excitation would appear to be mandatory for the [1,5] hydrogen migration are of A_2 and B_2 symmetry. Of course, these qualitative symmetry arguments strictly apply only to the parent BCP, not to the methyl-substituted analogues on which many of the experiments were conducted. On the other hand, experience from a variety of other domains of chemistry, including spectroscopic selection rules and the Woodward−Hoffmann analysis of pericyclic reactions, suggests that nominal destruction of symmetry elements by introduction of substituents is not usually sufficient to circumvent rules derived for the prototype.[41]

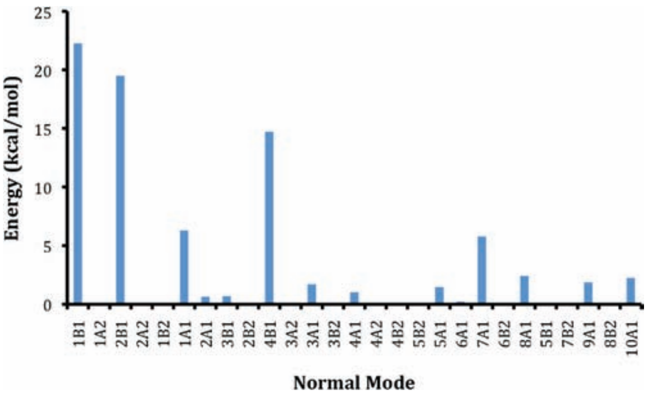


Figure 2. Histogram of energies in each normal mode of cyclopentadiene, arising from the ring-opening of BCP. Modes are identified by their symmetries and are ordered from left to right in increasing frequency.

The possible conflict between the experimental observations and the symmetry issues just discussed served to define the questions that formed the basis of the present study:

(1) Does the very fast [1,5] hydrogen migration that seems to be implied by the experiments on 2-MeBCP ring-opening in solution require reaction on a time scale comparable to that for IVR?

(2) If the answer to the first question is in the affirmative, does it follow that statistical kinetic models will be inadequate for describing the chemistry fully?

(3) If the answer to the second question is in the affirmative, what is the origin of the nonstatistical dynamics, and how does the system manage to circumvent the seeming symmetry-imposed prohibition on mode coupling?

■ RESULTS AND DISCUSSION

A Note on Tunneling. Calculations by Shelton and coworkers[42] have provided persuasive evidence that quantum mechanical tunneling plays an important role in the [1,5] hydrogen migration in cyclopentadiene. In the calculations described below, no tunneling contributions have been included. It would have been possible to do so in the master-equation calculations, but it would have been much more involved to include tunneling in the molecular dynamics simulations. More importantly, the comparison of results from the two approaches would then have become complicated by concerns about whether the two tunneling corrections were equivalent, and so answers to the principal questions outlined in the Introduction could have become obscured. The decision to neglect tunneling presumably means that the total rate constant for hydrogen migration is likely to be underestimated. Because a crucial parameter in assessing the adequacy of statistical models is the ratio of rate constants for reaction and for IVR,[43] the effect of underestimating the reaction rate constant on the overall analysis would be to make the system look more statistical than it really is.

Investigation of Symmetry Effects. To gain qualitative insight into the expected symmetry effects, we consider a single molecular dynamics trajectory, which was run from the BCP ring-opening transition structure without any initial kinetic energy

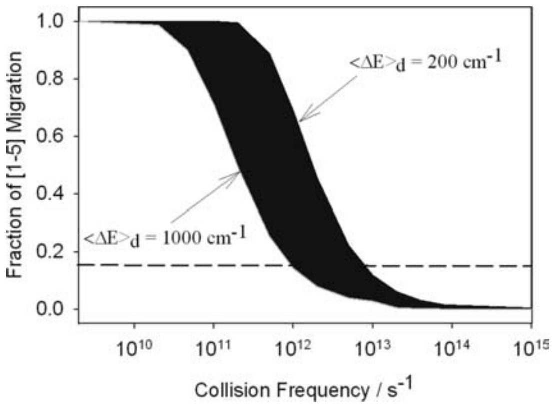


Figure 3. Yield of cyclopentadiene product having experienced a [1,5] hydrogen migration prior to complete collision cooling, as a function of collision frequency and average energy loss per collision. The shaded region represents the results obtained in the ME model using the limits of 200 and 1000 cm^{-1} for the average energy lost per collision. The horizontal dashed line corresponds to the estimated yield of rearrangement in solution, from the experiments on 2-MeBCP.

(even zero-point energy), aside from 0.5 kcal/mol in the reaction coordinate to get things moving. As soon as the carbons of the ring achieved planarity, which occurred at 38 fs, the trajectory was stopped, and the geometry and atomic momenta were expressed as linear combinations of the harmonic normal modes for CP.[44] By this device, it was possible to deduce the amount of energy deposited into each mode of CP as a result of the ring-opening reaction. The results are summarized in the histogram of Figure 2.

An analysis of this kind cannot be quantitatively exact, because of the errors associated with the use of the harmonic approximation in the treatment of highly excited vibrations. The magnitude of the error can be assessed by an energy-conservation analysis. At the BS-UB3LYP/3-21G level[45] used for the underlying potential energy surface, the ring-opening transition structure was calculated to have a potential energy 77.7 kcal/mol above that of CP at its equilibrium geometry. With the additional 0.5 kcal/mol of initial kinetic energy, the total energy in the CP modes should be 78.2 kcal/mol. In fact, the normal-mode analysis assigned a total of 80.9 kcal/mol, implying an error of ~5% arising from use of the harmonic approximation.

As expected, none of the A_2 or B_2 modes of CP was found to be excited, confirming the original expectation. In addition, the A_1 and B_1 modes were found to receive very unequal initial distributions of energy, with just three modes ($1B_1$, $2B_1$, and $4B_1$) acquiring 70% of the total. The identities and significance of these modes are discussed in the molecular dynamics section below.

Although one might anticipate that the results in a more realistic simulation would be complicated by the additional energy in each mode, characteristic of zero-point motion and thermal energy, ensemble averaged results from 190 quasiclassical trajectories (given in the Supporting Information) gave energy distributions, which were nearly identical to those discussed above. Presumably this arises because of the large magnitude of the kinetic energy released upon ring-opening. The only notable difference between the ensemble averaged quasi-classical results and those shown in Figure 2 is that each mode has at least zero-point energy.

Master Equation Analysis of the Reaction. Reanalysis (see the Supporting Information) of the experimental data[32] on solution-phase ring-opening of 2-MeBCP reveals that the formation of 1-MeCP occurred with a rate constant that was ~9% of that for the collisional cooling of 2-MeCP*. It should be noted, however, that [1,5] hydrogen migration in 2-MeCP* can occur in two ways, only one of which leads to 1-MeCP; the other is degenerate, and hence invisible. Consequently, we estimate that the total rate constant for [1,5] migrations in 2-MeCP* must have had a magnitude of 15–20% that for collisional cooling.

Master-equation analysis of the BCP ring-opening scheme shown in Figure 1 was carried out with the MESMER code[46] (see the Supporting Information for details), to explore the effect of stepwise collisional relaxation on the competition between collisional cooling and reaction of 2-MeCP* across the manifold of its energetically accessible rovibrational states. MESMER is a freely available, open source, object oriented C++ program for carrying out ME calculations and performing eigenvalue-eigenvector analysis on arbitrary multiple well systems. The master equation analysis in this work relies on RRKM theory for treating the BCP→CP and CP→CP isomerization rate coefficients, and an isolated-binary-collision (IBC) model for treating collisional deactivation/activation processes that arise through interactions between solute and solvent in the liquid phase. The validity of the IBC model for liquids has been questioned, but recent analysis suggests that it should be adequate for the qualitative conclusions required in the present application.[47,48] Effective collision frequencies between 10^9 and 10^{15} s^{-1} were considered, with the average energy loss per collision between 200 and 1000 cm^{-1} (0.6–2.9 kcal/mol). The results are summarized in Figure 3.

Assuming that the experimental results found for 2-MeBCP would be similar for BCP itself, one can see that the observed yield of cyclopentadiene that has undergone a [1,5] hydrogen migration (horizontal line in Figure 3) is consistent with an IBC collision frequency of 10^{12}–10^{13} s^{-1} and an energy loss per collision within the range considered. In other words, a statistical model seems capable of explaining the observed results without the need to invoke unusual effects or unusual values for parameters. The only caveat to this conclusion might be the neglect of tunneling, mentioned earlier.

Molecular Dynamics Simulation. A device that has been used to good effect in other studies of nonstatistical dynamics is to enquire whether static equilibrium symmetries of reactive intermediates are expressed in the ratio of the products derived from them.[9,49–51] This is frequently a more sensitive test than the comparison of observed rate constants with those calculated from a statistical model. In the present example, the question was whether any difference in propensity could be detected for [1,5] migration of the two methylene hydrogens in the chemically activated cyclopentadiene. In the C_{2v} equilibrium geometry of cyclopentadiene, the methylene hydrogens are related by symmetry, and so any statistical kinetic model must assign to each of them exactly equal probability for migration. However, under circumstances where the statistical approximation fails, the symmetry of the PES need not be expressed in the final product ratio.[20]

Using the Gaussian 03[52] suite of programs, Born–Oppenheimer direct dynamics were run at the BS-UO3LYP/3-21G[53] level, which, of the methods tested, offered the best compromise between speed and agreement with the known thermochemistry of BCP and CP (see the Supporting Information). Trajectories were initiated starting from the ring-opening transition state, and initial kinetic energy distributions were selected by quasiclassical random phase normal-mode

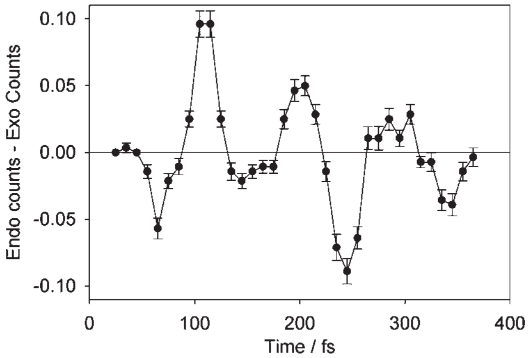


Figure 4. Time dependence of the exo and endo [1,5] H migrations. The *y*-axis in the plot gives the difference between endo and exo counts for a particular 10 fs time bin, and the results are normalized to the total number of H shift events. Error bars were obtained assuming Poisson statistics.

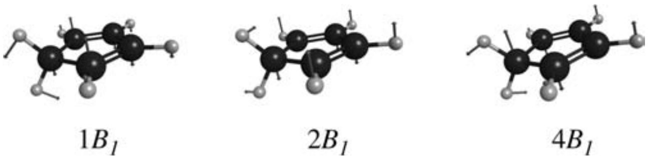


Figure 5. The three normal modes of cyclopentadiene that receive most of the kinetic energy resulting from BCP ring-opening (see Figure 2).

sampling from a canonical ensemble.[54] Recent work suggests that this sampling procedure gives post-TS dynamics, which are statistically indistinguishable from those obtained using Wigner sampling procedures.[55] Phase angles between normal modes were fully randomized, implying that starting structures were displaced from the exact transition-structure stationary point. Rotations were treated classically. Details and a sample input file are given in the Supporting Information.

To ensure that the results were independent of the algorithms used for initial-state sampling and trajectory propagation, several hundred trajectories were also calculated using a version of the VENUS dynamics package,[56,57] which we have locally modified to interface with several electronic-structure programs. As described in the Supporting Information, the results were statistically indistinguishable from those obtained with the Gaussian 03 molecular dynamics routines, and so the data from the two simulations were combined to make the graph in Figure 4.[58]

Simulations of the reaction at a typical experimental temperature of 303 K afforded no molecules undergoing the [1,5] hydrogen shift with the 370 fs time limit set for each trajectory. It would have been possible to run the trajectories longer, but there are then concerns about the zero-point energy “leakage” that inevitably occurs eventually in any quasiclassical trajectory simulation.[59] The absence of migrations may well be due to the neglect of tunneling, mentioned above.

To accumulate sufficient trajectories showing hydrogen migration to allow meaningful statistical analysis, the reaction was simulated at temperatures significantly above the experimental value, 1000, 1500, and 2000 K. The respective extents of [1,5] hydrogen migration were found to be 2.1%, 6.4%, and 12.1%. The migrations were characterized by whether the hydrogen that had been originally endo or exo in the BCP reactant underwent the shift. The endo:exo ratio was found to be 1.0:1, 1.0:1, and 1:1.1 at the three temperatures. The obvious interpretation of these MD results was that they were showing statistical behavior. This conclusion was reinforced by computing the overall rate constant for migration from 1998 trajectories at 2000 K, which was found to be 3.5×10^{11} s^{-1}, to be compared to 3.1×10^{11} s^{-1} from the MESMER[46] (statistical RRKM) calculations.

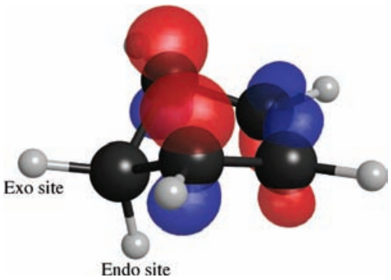


Figure 6. A π MO of bent cyclopentadiene, illustrating the better orbital alignment for [1,5] migration of a hydrogen from an endo site.

However, a very different picture emerged from examining the time-dependence of the endo and exo shifts observed at 2000 K (Figure 4). The near unit final ratio of endo:exo migrations was found to mask the fact that, in certain time windows, the preference for migration of one hydrogen over the other could be as big as ~10:1.

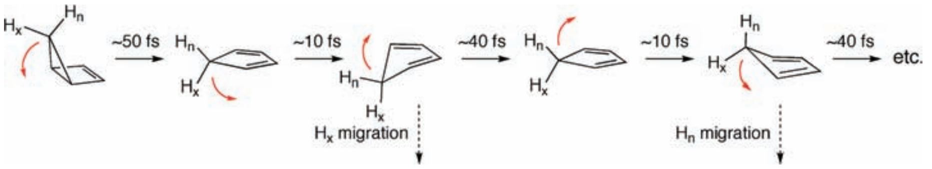
Analysis of the trajectories revealed that the oscillatory ratio of hydrogen migrations was associated primarily with the $1B_1$ vibrational mode of cylopentadiene, which was one of those heavily excited by the ring-opening reaction. This mode, as well as the other two ($2B_1$ and $4B_1$) found to receive most of the initial kinetic energy from the ring-opening reaction, are shown in Figure 5. The $1B_1$ vibration bends the methylene carbon out of the plane of the ring. The $2B_1$ and $4B_1$ modes are primarily out-of-plane bending modes of the vinyl hydrogens. They appear to be only indirectly involved in the H-migration dynamics: they mix with and thereby modulate the $1B_1$ motion of the ring.

In the Supporting Information, we show a plot of the ensemble-averaged kinetic and potential energy in the $1B_1$ mode, which clearly demonstrates its damped oscillatory behavior.

The reason for the strong dependence of the hydrogen migration on the $1B_1$ vibration could be understood when it was discovered that hydrogen migrations in the bent cyclopentadiene occurred almost exclusively from an endo site. This is presumably because the endo C−H bond has a better alignment with the orbital at the migration terminus (Figure 6). Excursions of the ring bend brought each methylene hydrogen in turn into the preferred migration position, leading to the oscillatory migration behavior (Scheme 2).

Further insight into the relationship between the ring-opening and hydrogen migration dynamics came from a Fourier analysis. Two geometrical parameters were used to characterize the ring-opening reaction: the distance between the two carbons constituting the bridgeheads of BCP, and the out-of-plane bend angle arising from the $1B_1$ vibration. Respective averaged distance−distance and angle−angle correlation functions for these parameters were computed from the set of trajectories that led to a [1,5] H shift.[4] The Fourier transforms were then taken, with the results shown in Figure 7. The transformed correlation functions showed peaks corresponding to bending modes of the methylene hydrogens. However, these CH_2 bending-mode peaks were

Scheme 2. Schematic Summary of Trajectory Results



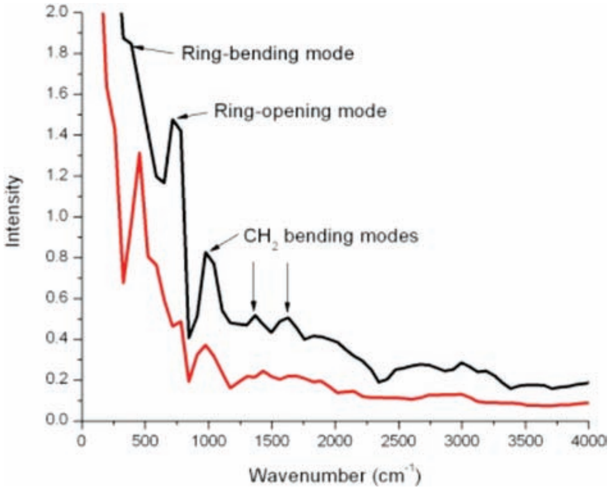


Figure 7. Fourier transforms of correlation functions for the BCP→CP trajectories that led to [1,5] H shift. The red curve corresponds to the out-of-plane bend angle, and the black curve corresponds to the distance between the bridgehead atoms.

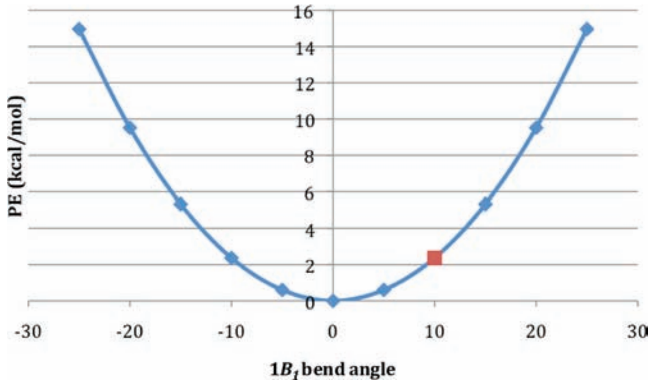


Figure 8. BS-O3LYP/3-21G potential energy of cyclopentadiene as function of bending in the $1B_1$ coordinate. The red “■” shows the average bend angle at which [1,5] hydrogen shifts occur in the MD simulations at 2000 K.

absent when similar analysis was carried out on trajectories that failed to result in [1,5] H migration (see the Supporting Information).

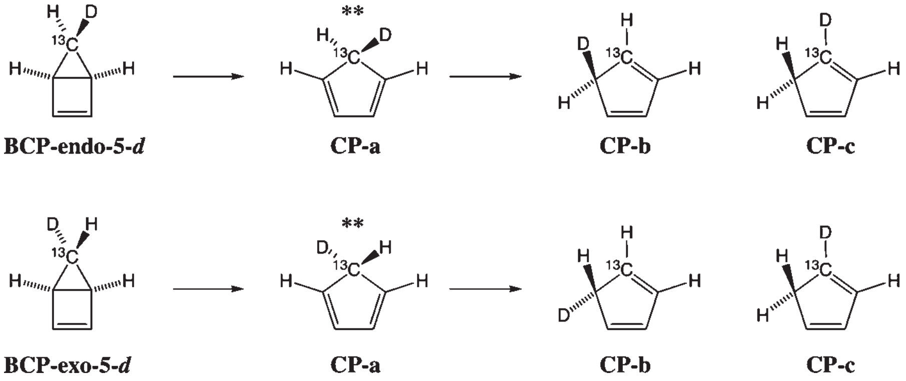
Origins and Significance of the Nonstatistical Dynamics. One of the questions raised in the Introduction was how this system could circumvent the seeming symmetry-imposed prohibition on mode coupling. Another arises following the detailed analysis of how the effect is manifested: if the dynamics have no influence on the overall rate of the reaction, or on the overall selectivity of methylene hydrogen migration, is there any real significance to the discovery? In this section, possible answers to both questions are offered.

On the symmetry question, two hypotheses might be offered. One is based on the recognition that a vibrating polyatomic molecule has a structure matching the stationary-point symmetry only on average. At any instant, it will almost always have only C_1 symmetry. Consequently, rules derived from higher, time-averaged symmetries may not be rigorously obeyed. However, this argument is akin to the one raised earlier, which would make any molecular symmetry rules in chemistry seem to be susceptible to circumvention by the trivial device of introducing a substituent that makes the molecule asymmetric. Because experience reveals that the essence of the rule is usually preserved even when the formal symmetry is destroyed,[41] invoking an arbitrary exception in this case does not constitute a very satisfactory explanation.

The second hypothesis is that because the high-amplitude bending motion illustrated in Scheme 1 opens a particularly favorable channel for migration of a hydrogen from an endo site (Figure 6), there may be enough thermal energy in the A″ modes to surmount the migration barrier, without need for direct mode coupling. Supporting this latter view is the fact that trajectories started with 10−20 kcal/mol additional energy in the methylene bending modes afforded more than twice as many migrations as normal, whereas a similar amount of energy added to other C−H bending modes had no effect.

If correct, this hypothesis could have broader implications. At all levels of theory that we have investigated, the transition structure for [1,5] hydrogen migration in cyclopentadiene has a flat, or very nearly flat, ring of carbon atoms. Why, then, do the hydrogen migrations occur from the endo face of a bent ring in the MD simulations? The answer appears to be the following: as described above, the methylene C−H bond in the endo site of a bent ring has a particularly favorable orbital alignment with a π orbital on the migration terminus for the [1,5] shift, better even than in the planar ring seen in a “normal” migration TS. However, for a thermally activated reaction, the reduction in barrier height that comes from this better overlap is insufficient to compensate for the energetic penalty that has to be paid to bend the ring in the first place. By contrast, in a cyclopentadiene that has just been generated by BCP ring-opening, there is already a large amount of energy deposited in the ring-bending mode (~20 kcal/mol, according to the analysis summarized in Figure 2), and so the penalty does not have to be paid. The implication of this conclusion is that intermediates reacting under the influence of nonstatistical dynamics may not only eschew the lowest-barrier exit channel,[4] but they can even choose pathways that do not correspond to passage through conventional transition states at all. In the present example, the dynamically favored path for [1,5] hydrogen migration appears to be some way up the wall of a valley, when projected onto the ring-bending coordinate (Figure 8). This effect has some

Scheme 3. Proposed Use of Isotopic Labels To Test the Predictions of the MD Simulations[a]



[a] See text for discussion.

similarity to the recently described "roaming reactions", which also seem to skirt conventional transition states.[60,61]

Finally, one may wonder whether the oscillations depicted in Figure 4 and Scheme 2 are of any importance if they have no significant influence on the kinetics or overall propensity for migration of the exo and endo methylene hydrogens. We believe they are, for the following reason. The asymmetry in migration of exo and endo hydrogens in this reaction should increase as the damping of the oscillations increases. This effect is best illustrated with a simple model, in which the oscillatory behavior depicted in Figure 4 is approximated by a damped sine wave:

$$y = \sin(\omega t)e^{-kt}$$

where ω is the oscillation frequency and k is a rate constant for loss of amplitude in that mode (by combined intra- and intermolecular energy transfer). When ω is in units of Hz and k in s^{-1}, the overall product ratio in this model system is $e^{k/2\omega}$ (see the Supporting Information). For a 300 cm^{-1} vibration with $k = 10^{12}$ s^{-1}, a typical value for intramolecular vibrational energy redistribution,[35,36] the product ratio is 1.06. However, if k were raised to 10^{13}, as might happen in a solvent, the ratio becomes 1.7. Of course, this increased selectivity comes at the price of a lower overall yield, but the effect could still be detectable, as we describe in the next section. It is perhaps worth emphasizing that collisions between solute and solvent would be expected to perturb both inter- and intramolecular energy distributions, and that both would be expected to lead to the damping effect we seek. It seems safe to assume that the effective k for damping would be bigger than that for pure intermolecular energy transfer.

Proposed Experimental Test. The key prediction from the MD simulations, which would be susceptible to experimental test given some significant synthetic effort, is that selective deuterium labeling of the exo and endo methylene hydrogens of BCP should lead to different deuterium distributions in the cyclopentadiene products, and that this effect could be bigger in the solution phase than the gas phase. An experiment that could detect this effect is shown in Scheme 3. According to any statistical kinetic model, the two chemically activated cyclopentadienes, **CP-a**, in Scheme 3 are identical in all respects, and hence the ratio of [1,5] migration products **CP-b**:**CP-c** must be identical, also. However, the prediction from the MD simulations is different. Increased damping of the $1B_1$ oscillation (as would occur on changing the reaction medium from gas phase to solution phase, and might occur on changing from one solvent to another) should cause the total yield of the products **CP-b** and **CP-c** to decrease, but the difference in ratio of **CP-b**:**CP-c** found from the two stereoisomeric BCP reactants to increase. Note that this experiment does not depend on any knowledge of the isotope effect on H versus D migration, because the isotope effect should be identical in the two experiments if statistical kinetic models were valid, and hence could not provide an explanation for a difference in **CP-b**:**CP-c** ratio seen in the two experiments. The approximations used in the models (neglect of tunneling, neglect of explicit solvent in the MD simulation, etc.) do not allow quantitative predictions to be made, but the qualitative effect should be clear and, if detected, should provide unambiguous evidence for the nonstatistical effects found in the present work.

■ CONCLUSIONS

The answers to the questions raised in the Introduction are that at least some of the chemically activated cyclopentadiene molecules generated by bicyclo[2.1.0]pentene ring-opening do seem to undergo [1,5] hydrogen migration before IVR is complete and that this does lead to nonstatistical dynamical effects. These are seen not in the overall kinetics or branching ratios, but in a predicted oscillatory preference for migration of the two methylene hydrogens. The favored explanation for how the system circumvents the seeming symmetry prohibition on mode coupling is that the modes excited by the ring-opening, particularly the $1B_1$ ring bend, open a new pathway for the [1,5] shift that can be accessed with just normal thermal energy in the A_2 and B_2 modes needed to form the migration reaction coordinate. The new migration pathway apparently does not involve a conventional transition state at all, but instead crosses the ridge between reactant and product part way up the "wall" of the $1B_1$ bending coordinate. Similar phenomena may well be common in other reactions where nonstatistical dynamics play an important role.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Computational details and the full citation for ref 52. This material is available free of charge via the Internet at http://pubs.acs.org.

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