Calculations Predict That Carbon Tunneling Allows the Degenerate Cope Rearrangement of Semibullvalene to Occur Rapidly at Cryogenic Temperatures

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ABSTRACT

Calculations on the role of tunneling in the degenerate Cope rearrangements of semibullvalene (1) and barbaralane (3) predict that, at temperatures below 40 K, tunneling from the lowest vibrational level should make the temperature-independent rate constants \( k = 1.43 \times 10^{-3} \text{ s}^{-1} \) and \( k = 7.28 \times 10^{-9} \text{ s}^{-1} \), respectively. An experiment, using semibullvalene-2(4)-d1, is proposed to test the prediction of rapid tunneling by 1 at cryogenic temperatures.

Tunneling in chemical reactions by hydrogen and its isotopes is relatively common, on account of their low masses.1 In contrast, reactions involving tunneling by heavier atoms, such as carbon, are comparatively rare.1b Reactions in which there is strong evidence for tunneling by carbon include the ring closure reactions of cyclopentane-1,3-diyl2 and cyclobutane-1,3-diyl,3 the automerization of cyclobutadiene,4 and the ring expansions of 1-methylcyclobutylfluorocarbene5 and noradamantylchlorocarbene.6 Experimental evidence, which supports the prediction that tunneling should play an important role in the ring-opening reaction of cyclopropylcarbinyl...
radical at low temperatures\textsuperscript{7} has very recently been obtained by James and Singleton.\textsuperscript{8}

In this communication, we report the results of calculations that predict tunneling by carbon should allow the Cope rearrangement of semibullvalene (1, Scheme 1) to occur rapidly at cryogenic temperatures. We also propose a possible way to test this prediction experimentally.

Since the first synthesis of 1\texttext{a} by Zimmerman et al.,\textsuperscript{9} more than four decades ago, semibullvalene has fascinated chemists because it undergoes a degenerate boat Cope rearrangement with an enthalpic barrier of only $\Delta H^\ddagger = 5.0 \pm 0.2$ kcal/mol.\textsuperscript{10,11} The low barrier height is one reason why 1 might be a good candidate for undergoing this reaction rapidly at cryogenic temperatures by tunneling.\textsuperscript{1}

However, even more important than the low barrier height for facilitating tunneling in the degenerate rearrangement of 1 is the narrowness of the reaction barrier.\textsuperscript{1,7} In breaking the cyclopropane ring bond, the distance between the carbons that form this bond increases by only about 0.86 Å.\textsuperscript{12} On the other hand, in forming the same type of bond at the other end of the molecule, the distance between another pair of carbons must decrease by this amount. Therefore, as in the case of the automerization of cyclobutadiene,\textsuperscript{4} two pairs of carbons must move, in order for the degenerate Cope rearrangement of 1 to occur. Consequently, in both reactions, either the effective tunneling mass is $2 \times 12 = 24$ (or 26, if the hydrogens attached to the carbons are included) or, equivalently, the effective width of the barrier through which tunneling occurs is a factor of $\sqrt{2}$ larger than the tunneling distance for just one pair of carbons.\textsuperscript{13}

To carry out tunneling calculations on the degenerate Cope rearrangement of 1, we performed electronic structure calculations on this reaction with the B3LYP functional\textsuperscript{14} and the 6-31G(d) basis set.\textsuperscript{15} It was already known that the B3LYP/6-31G(d) enthalpy of activation of $\Delta H^\ddagger = 4.5$ kcal/mol\textsuperscript{12} is in good agreement with the experimental values of $\Delta H^\ddagger = 5.0 \pm 0.2$ kcal/mol.\textsuperscript{10} Quantum effects on the reaction dynamics were computed semiclassically, using the small-curvature tunneling (SCT) approximation.\textsuperscript{16} The direct dynamics calculations were carried out with GAUSSRATE\textsuperscript{17} as the interface between Gaussian 03\textsuperscript{18} and POLYRATE.\textsuperscript{19}

Our results are displayed graphically in the Arrhenius plots shown in Figure 1. The points on the black line were computed using conventional transition state theory (TST),\textsuperscript{20}

\begin{figure}[!h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Arrhenius plot of the TST and TST + SCT rate constants for the Cope rearrangement of semibullvalene from 40 to 400 K.}
\end{figure}

\begin{table}[!h]
\centering
\begin{tabular}{|c|c|}
\hline
Parameter & Value \tabularnewline \hline
\hline
$\Delta H^\ddagger$ (kcal/mol) & 5.0 \pm 0.2 \tabularnewline \hline
\hline
\end{tabular}
\caption{Calculated enthalpy of activation for the Cope rearrangement of semibullvalene.}
\end{table}

\textsuperscript{13} The imaginary frequency that is associated with tunneling through a parabolic reaction barrier is inversely proportional to both the width of the barrier and the square root of the effective mass. Therefore, either increasing the barrier width by $\sqrt{2}$ or doubling the effective mass decreases the imaginary frequency by a factor of $\sqrt{2}$. Hence, either change has the same effect on reducing the probability of tunneling. (See ref 1a).


\textsuperscript{17} Frisch, M. J. et al. \textit{Gaussian 03}, revision D.02; Gaussian, Inc.: Wallingford, CT, 2004. The full reference is given in the Supporting Information.

\textsuperscript{18} Corchado, J. C. et al. \textit{POLYRATE-version 9.5}; University of Minnesota: Minneapolis, MN, 2007. The full reference is given in the Supporting Information.
and the points on the red line were computed by TST, with inclusion of SCT.

At temperatures down to 100 K, the two types of calculations can be seen to provide almost identical results. For example, at 100 K, k(TST + SCT) = 5.48 × 10^8 s⁻¹, which is only a factor of 1.8 larger than k(TST). At 100 K, the calculated activation parameters are also almost the same—Eₐ = 4.43 kcal/mol and log A = 12.37 s⁻¹ with inclusion of tunneling, and Eₐ = 4.71 kcal/mol and log A = 12.72 s⁻¹ without it. Tunneling increases the reaction rate by lowering the average energy at which molecules can react. However, as shown by the relative sizes of the A factors, the probability of passing over it is only a factor of 1.8 larger than the change of 0.75 Å in the degenerate rearrangement of 3, whereas the rate of degenerate rearrangement of 1 is too slow to be detectable below 100 K.

As can be seen in Figure 1, below 100 K the curvature in the TST + SCT Arrhenius plot becomes obvious. As the temperature is decreased below 100 K, not only do more molecules react by tunneling, but also more molecules tunnel from the lowest vibrational level of the reactant. Below 40 K, k(TST + SCT) becomes essentially temperature independent (i.e., Eₐ = 0), as all the reacting molecules tunnel from the lowest vibrational energy level.

At 40 K, k(TST + SCT) = 1.43 × 10⁻³ s⁻¹, so from this temperature down to 0 K, the half-life of the degenerate rearrangement of semibullvalene is calculated to be 485 s ≈ 8 min. Without tunneling, TST predicts that at 40 K the half-time for reaction would be a factor of 10¹⁰ longer.

We also have carried out TST + SCT calculations on the degenerate Cope rearrangement of barbalanone (3). The value of ΔH¹ = 7.3 kcal/mol, which has been measured for this reaction, is 2.3 kcal/mol higher than the value of ΔHᵗ = 5.0 ± 0.2 kcal/mol, which has been measured for degenerate rearrangement of 1 at somewhat lower temperatures. In good agreement with experiment, B3LYP/6-31G(d) calculations, without any tunneling corrections, give 1.9 kcal/mol for the difference in ΔHᵗ values.

B3LYP/6-31G(d) calculations also find that, on breaking the cyclopropane ring bond in the degenerate rearrangement of 3, the change in C–C distance of 0.82 Å is 0.07 Å larger than the change of 0.75 Å in the degenerate rearrangement of 1. This result suggests that the barrier to degenerate rearrangement is not only higher but also wider in 3 than in 1. Consequently, tunneling through the barrier should be slower for 3 than for 1.

Indeed, at 40 K, the rate constant for tunneling in the degenerate rearrangement of 3 (Scheme 2) is computed to be k(TST + SCT) = 7.28 × 10⁻⁹ s⁻¹. This rate constant is 5.09 × 10⁻⁵ smaller than the rate constant for tunneling in the degenerate rearrangement of 1. At 40 K, the half-time for rearrangement is computed to be 8.7 years for 3, compared to about 8 min for 1. Thus, our calculations predict that the slightly higher and wider barrier for degenerate rearrangement of 3 than for 1 should make the rate of degenerate rearrangement of 3 at 40 K too slow to measure, whereas the rate of degenerate rearrangement of 1 at 40 K by tunneling is predicted to be fast enough to be easily measurable.

The rate of degenerate rearrangement of 1a can be obtained by NMR line-shape analysis at temperatures above 100 K, but below 100 K, the rate of this reaction is computed to be too slow to affect the NMR spectrum of 1a. Isotopic labeling, as in 1b or 1d, might provide a way to follow the rates of their Cope rearrangements at 40 K, but it would be important first to know how large the kinetic effects of isotopic substitution in 1a are likely to be. Therefore, we carried out calculations on the effects of isotopic substitution on the rate of Cope rearrangement of 1 at 40 K.

Some H/D and ¹²C/¹³C kinetic isotope effects (KIEs) on the Cope rearrangement of 1, calculated by TST + SCT at 40 K, are given in Table 1. Calculations at lower temperatures typically eliminate the same results because, again, below 40 K all of the reaction occurs by tunneling from the lowest vibrational level of not only 1 but also of its isomers.

As would be expected, substitution of ¹³C for ¹²C at the terminal atoms of 1 is predicted to slow the rate of rearrangement. The KIE for substitution of ¹³C for ¹²C at all four terminal carbons, as in 1e, is almost exactly the square of the KIE for substitution of ¹³C for ¹²C at just one end of 1, as in 1d.

Although the KIE for substitution of D for H at all four terminal carbons (as in 1e) is also computed to be normal, the KIE for substitution of D for H at just one end of 1 (as in 1b) is calculated to be inverse. In other words, despite the greater mass of two deuterons, compared to two hydrogens,
1b is predicted to tunnel faster than 1a by a factor of 1/0.73 = 1.37. This is, to the best of our knowledge, only the second prediction of a large inverse KIE on the rate of a tunneling reaction.27

The inverse KIE, predicted for substitution of deuteria for hydrogens in 1b, but not in 1c, is readily explicable. Replacement of H by D is computed to make the Cope rearrangement of 1b to 2b exothermic by 0.17 kcal/mol at 40 K. As is usually the case for equilibrium isotope effects, the higher C–H bending frequency at carbons that are nominally sp3, rather than sp2, makes the zero-point energy lower in 2b than in 1b.28

The exothermicity of the conversion of 1b to 2b is calculated not only to make the effective barrier height to Cope rearrangement lower in 1b than in 1a by about 0.04 kcal/mol at 40 K but also to narrow the barrier. The lowering and narrowing of the barrier, through which tunneling must occur, is calculated to make the rate of tunneling faster in 1b than in 1a by a factor of 1.37 below 40 K, despite the larger effective tunneling mass in 1b.

Of course, the free energy change for rearrangement of 1c to 2c, like that for the rearrangement of 1a to 2a, is zero. Therefore, the only difference between the degenerate rearrangements of 1a and 1c is the greater effective tunneling mass in the rearrangement of 1c. As shown in Table 1, this difference is computed to result in a normal KIE of k(1a)/k(1c) = 2.03.

Although 13CH and 12CD have the same mass, Table 1 shows that the isotopic substitution of 13C for 12C in 1e is computed to produce a 2.78 times larger KIE on tunneling than substitution of H for D in 1c. In the cleavage of the C2–C8 bond and the forming of the C4–C6 bond of 1, the carbons are computed to move about 0.19 Å more than the hydrogens attached to them. Therefore, the isotopic substitution of 13C for 12C as in 1e would, indeed, be expected to have a larger effect than the isotopic substitution of D for H as in 1c, on retarding the rate of tunneling by increasing the effective mass that tunnels.

It might be possible to measure the rate of rearrangement of 1b to 2b at cryogenic temperatures by taking advantage of the fact that this reaction is nondegenerate and has ΔG ≈ −0.17 kcal/mol at both high and low temperatures. At 298 K, this small free energy difference corresponds to an equilibrium constant for formation of 2b from 1b of only K = 1.25. However, this equilibrium constant increases to K = 8.48 at 40 K and to K = 5260 at 10 K. Therefore, if the 5:4 equilibrium mixture of 2b to 1b at room temperature was rapidly deposited on the window of an IR cell, maintained at 10 K, the rate of Cope rearrangement of 1b to 2b could be measured by monitoring the rate of disappearance of 1b, as the equilibrium mixture of 5260:1 of 2b:1b was established at cryogenic temperatures.29

This experiment could actually be performed on an equilibrium mixture of semibullvalene-2-d1 and 4-d1 since at 10 K the former isopomer is predicted to dominate the latter by a ratio of 74:1. Askani has, in fact, reported the synthesis of 1,5-dimethylsemibullvalene-2-(4)-d1.30 Using this derivative of 1, an experimental test of our prediction that tunneling should allow semibullvalene to undergo rapid Cope rearrangement at cryogenic temperatures could be attempted.31

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Supporting Information Available: The optimized B3LYP/6-31(d) geometries and energies for 1 and 3, the transition structures for their degenerate Cope rearrangements, and the TST and TST + SCT rate constants for this reaction. This material is available free of charge via the Internet at http://pubs.acs.org.