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Tunneling in the 1,5-Hydrogen Shift Reactions of 1,3-Cyclopentadiene and 5-Methyl-1,3-Cyclopentadiene

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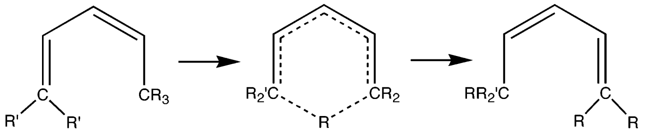
Abstract: MPW1K/6-31+G(d,p) calculations which include the effects of small curvature tunneling find that, around room temperature, thermally activated tunneling dominates the 1,5-hydrogen shift reactions of 1,3-cyclopentadiene (**2a**) and 5-methyl-1,3-cyclopentadiene (**2c**). The calculated temperature dependence of the H/D kinetic isotope effect (KIE) for the latter rearrangement agrees well with experimental measurements that were published nearly 40 years ago. It is argued that the experimental KIEs provide prima facie evidence for tunneling in this reaction. The calculations also predict that it should be possible, at least in principle, to confirm this conclusion by observing curvature in the Arrhenius plot for the rearrangement of **2c**.

Introduction

In 1966, Roth and König published an experimental study of the 1,5-shift of hydrogen in *Z*-1,3-pentadiene (**1a**).[1] They measured the kinetics of the rearrangement of *Z*-1,3-pentadiene-d_2 (**1b**), and they also obtained the primary H/D kinetic isotope effect (KIE) for this reaction by measuring the kinetics of the rearrangement of **1c**. However, four decades later, the role played by tunneling in this and similar reactions remains a subject of discussion in the literature.



1a, R = R' = H
1b, R = H, R' = D
1c, R = D, R' = H

1a, R = R' = H
1d, R = H, R' = D
1e, R = D, R' = H

Evidence for thermally activated (vibrationally assisted)[2] hydrogen tunneling in this reaction comes from the large size of the KIE measured for it, especially when the KIE is extrapolated to room temperature. Many different types of electronic structure calculations have shown that the KIE, calculated for this reaction without inclusion of tunneling, is significantly smaller than the experimental value.[2,3] However, inclusion of multidimensional tunneling in semiempirical calculations brings the calculated KIE into good agreement with the value measured by Roth and König.[4]

Nevertheless, Doering and Zhao have recently pointed out that seemingly modest uncertainties in experimental k_H/k_D values for 1,5-shifts of hydrogen in 1,3-pentadienes result in very large uncertainties when the KIEs are extrapolated to room temperature.[5] It has also been noted[5,6] that both ab initio[7] and B3LYP calculations,[8] performed without inclusion of tunneling corrections,[9] provide enthalpies of activation for the 1,5-shift of hydrogen in *Z*-1,3-pentadiene that are in excellent agreement with the value of $E_a^{\ddagger} = 36.3 \pm 0.5$ kcal/mol, measured by Roth and König.[1]

In a heroic attempt to find purely experimental evidence for tunneling in the Arrhenius plot of the rate constants for 1,5-hydrogen shift in a 1,5-diaryl-1,3-pentadiene, Doering and Zhao measured the rates of this reaction over a temperature range of 108°, from 77° to 185°.[5] However, they found no curvature in the Arrhenius plot over this temperature range and, hence, no indication of the occurrence of tunneling. In the absence of such direct experimental evidence for tunneling, Doering and Zhao wrote, "The tunneling effect is likely, in the opinion of some, to remain relegated to the virtual world of calculation."[5]

In this article, we report the results of calculations on the 1,5-hydrogen shifts in 1,3-cyclopentadiene (**2a**) and in 5-methyl-

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(9) When multidimensional tunneling is included in B3LYP/6-31G* calculations on the 1,5-hydrogen shift in *Z*-1,3-pentadiene, in the temperature range where this reaction was studied experimentally,[1] the calculated E_a is reduced by about 2.5 kcal/mol from the value computed without consideration of tunneling.[8] (Shelton, G. R.; Hrovat, D. A.; Borden, W. T. Unpublished results). Therefore, the good agreement of the B3LYP/6-31G* value of E_a, obtained without any correction for tunneling, with the value measured by Roth and König[1] is due to the tunneling correction fortuitously being nearly the same size as the amount by which B3LYP/6-31G* underestimates E_a for this reaction.

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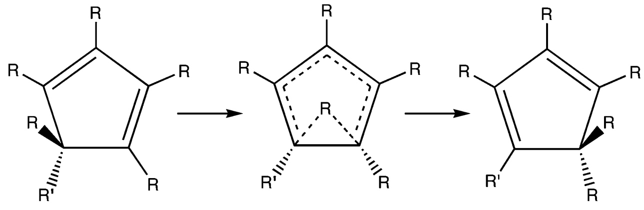
Table 1. Calculated Temperature Dependence of the Rate Constants (s^{-1}) $\times 10^7$ for [1,5]Sigmatropic Reactions of **2a** and **2b** and $\times 10^5$ for **2c** and **2d**[a]

reactant	260 K	280 K	300 K	320 K
2a[b]	1.31 (96.6%)	21.2 (93.0%)	274 (88.9%)	2780 (84.5%)
2b	0.111 (85.3%)	2.85 (80.0%)	49.8 (75.0%)	624 (70.3%)
k(**2a**)/*k*(**2b**)	11.8	7.44	5.50	4.46
2c[c]	1.95 (96.6%)	24.7 (92.0%)	248 (87.9%)	2000 (83.6%)
2d	0.175 (83.4%)	3.28 (78.1%)	43.4 (73.1%)	4250 (68.5%)
k(**2c**)/*k*(**2d**)	11.2	7.51	5.72	4.70
k(**2c**)/*k*(**2d**) measured[d]		7.67	5.75	4.45

[a] The percentage of each reaction that involves tunneling is shown in parentheses. The KIEs, *k*(**2a**)/*k*(**2b**) and *k*(**2c**)/*k*(**2d**), computed from the rate constants, are also given at each temperature, as are the KIEs that were measured for the rearrangement of **2c** and **2d**.[11] [b] At 240 K, $k = 0.0699 \times 10^{-7}$ s^{-1}, and 98.9% of the molecules that react do so by tunneling. [c] At 240 K, $k = 0.1271 \times 10^{-5}$ s^{-1}, and 98.2% of the molecules that react do so by tunneling. [d] Reference 11.

1,3-cyclopentadiene (**2c**). The nearest-neighbor relationship between the origin of and terminus for hydrogen migration in these compounds makes the reported activation energies for rearrangement of **2b** to **2e**[10] and of **2c** to **2f**[11] lower by, respectively, 12.0 and 14.6 kcal/mol than $E_a = 36.3$ kcal/mol for rearrangement of **1b** to **1d**.[1]

Our computational results show that the unusually strong temperature dependence, found by McLean and co-workers in the KIE for **2c** → **2f** and **2d** → **2g**, is due to a major contribution of tunneling to the rate of reaction of **2c**. We suggest that such strong temperature dependence provides prima facie experimental evidence for tunneling in this and other reactions. In addition, our calculations predict that curvature should be visible in an Arrhenius plot of the rate constants for the rearrangement of **2c**, thus suggesting another purely experimental way to confirm that tunneling in this reaction does not belong exclusively to "the virtual world of calculation".



2a, R = R' = H
2b, R = D, R' = H
2c, R = H, R' = CH_3
2d, R = D, R' = CH_3

2a, R = R' = H
2e, R = D, R' = H
2f, R = H, R' = CH_3
2g, R = D, R' = CH_3

Computational Methodology

For our calculations on the rearrangements of **2a**−**d**, energies, inclusive of vibrational contributions, were computed using density functional theory. Truhlar's MPW1K functional[12] and the 6-31+ G(d,p) basis set[13] were employed. Transition states were located using canonical variational transition state theory (CVT).[14] Quantum effects on the reaction dynamics were calculated with the small curvature tunneling (SCT) approximation.[4a,15] Direct dynamics calculations were carried out with GAUSSRATE[16] as the interface between Gaussian 03[17] and POLYRATE.[18]

Results and Discussion

The CVT + SCT rate constants, calculated for the [1,5]-sigmatropic shifts in **2a**−**d** in the temperature range between 260 and 320 K, are given in Table 1. Shown in parentheses at each temperature is the percentage of the rate constant that comes from tunneling through the energy barrier to reaction. The balance of the CVT + SCT rate constant is for passage over the barrier.

Table 1 shows that in all four compounds the majority of the [1,5]sigmatropic rearrangement is calculated to proceed by tunneling through the energy barrier, rather than by passage over it. Although the contribution of tunneling to the overall rate of reaction is smaller when the migrating atom is deuterium, rather than hydrogen, even for migration of deuterium most of the reaction is calculated to occur by thermally activated tunneling.

The data in Table 1 show that the rate constants for deuterium migration are more sensitive to temperature than the rate constants for hydrogen migration. This means that the 1,5-shifts of deuterium in **2b** and **2d** must have effective Arrhenius activation energies higher than the analogous shifts of hydrogen in, respectively, **2a** and **2c**. This is indeed the case, but, as shown in Table 2, the Arrhenius activation energies, particularly those for the 1,5-shift of hydrogen in **2a** and **2c**, are temperature-dependent.

The calculated E_a for the 1,5-hydrogen shift in **2a** decreases by 5.5 kcal/mol between 320 and 240 K. In contrast, E_a for the 1,5-deuterium shift in **2b** decreases by only 1.7 kcal/mol over this temperature range. The corresponding decreases in E_a for the rearrangements of **2c** and **2d** over the same 80° range are, respectively, 4.1 and 1.4 kcal/mol.[19]

It is tempting to attribute the decreases in both E_a and A, the Arrhenius pre-exponential factor, with decreasing temperature to increases in the percentage of molecules that cross the barrier as the temperature is lowered. However, the data in Table 1 shows that this explanation cannot be entirely correct. For example, between 260 and 240 K, the E_a for rearrangement of **2a** drops by 12.4%, but the number of molecules that tunnel increases by only 2.3%.

Instead, the major contributor to the decreases in both E_a and A with decreasing temperature is a decrease in the average

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(17) Frisch, M. J.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
(18) Corchado, J. C.; et al. *POLYRATE*, version 8.5.1; University of Minnesota: Minneapolis, MN, 2000.

Table 2. Calculated Activation Energies (E_a, kcal/mol) for the [1,5]Sigmatropic Reactions of **2a**−**d**, Obtained from the Local Slopes of Arrhenius Plots of the Computed Rate Constants between 240 and 320 K[a]

reactant	240 K	260 K	280 K	300 K	320 K
2a	16.9 (7.3)	19.3 (9.4)	20.8 (10.7)	21.8 (11.4)	22.4 (11.8)
2b	22.5 (11.0)	23.3 (11.7)	23.7 (12.0)	24.0 (12.3)	24.2 (12.4)
2b (measured from 343 to 363 K)[b]				24.3 ± 0.5 (12.1)[b,c]	
2c	16.0 (8.7)	17.8 (10.3)	18.9 (11.2)	19.6 (11.7)	20.1 (12.1)
2c (measured from 280 to 320 K)[d]				19.9 ± 0.3 (10.9)	
2d	20.5 (11.5)	21.0 (12.0)	21.4 (12.3)	21.7 (12.5)	21.9 (12.6)
2d (measured from 280 to 320 K)[d]				22.4 ± 0.1 (11.9)	

[a] The logarithm of the pre-exponential factor (log A, A in s^{-1}) is given in parentheses at each temperature. Also shown are the activation parameters derived from the experimental rate constants.[10,11] [b] Reference 10. [c] For comparison, at 353 K the calculated values are 24.5 (12.7). [d] Reference 11.

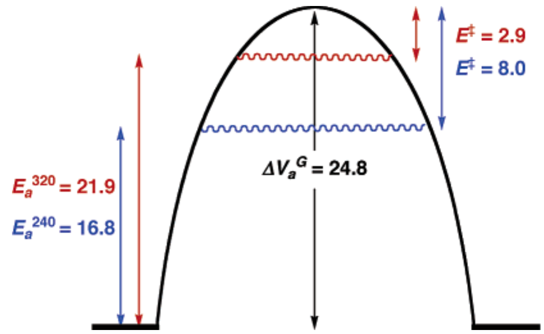

Figure 1. Schematic depiction of the effect of lowering the temperature from 320 to 240 K on thermally activated tunneling in **2a**. The vibrationally adiabatic barrier height (ΔV_a^G),[4a] the activation energy (E_a) for thermally activated tunneling at 240 and 320 K, and the approximate height ($E^‡$) of the effective barrier through which tunneling occurs at these two temperatures are all given in kcal/mol. Note that the E_a values shown for tunneling are slightly smaller than the overall E_a values given in Table 2, because the latter are weighted averages that include contributions from molecules that pass over the top of the barrier.

energy at which tunneling occurs. As less thermal energy is available, thermally activated tunneling occurs at energies that are farther below the top of the barrier. Consequently, as illustrated schematically in Figure 1, the effective height ($E^‡$) and, along with it, the effective width of the barrier through which tunneling occurs increase. Since increases in the effective barrier height and width both decrease the probability of tunneling,[20] A decreases, along with E_a for tunneling.

Because the E_a values for the rearrangements of **2a**−**d** between 240 and 320 K are predicted to be temperature-dependent, Arrhenius plots of the CVT + SCT rate constants for these rearrangements in this temperature range are not straight lines but are slightly curved. The Arrhenius plots that exhibit the greatest curvature are those for the rearrangements of **2a** and **2c**. These plots, which are displayed in Figure 2, appear linear at high temperatures, but a deviation from linearity is obvious in the low-temperature region between 240 and 260 K.

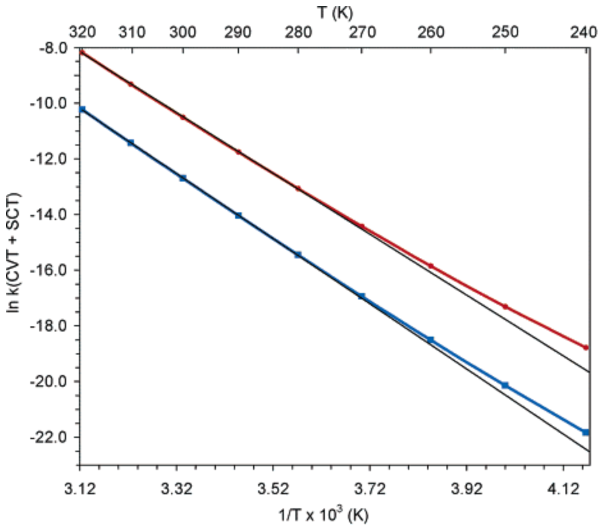

Figure 2. Arrhenius plots of the CVT + SCT rate constants for the rearrangements of **2a** (blue) and **2c** (red) at 10° temperature intervals, in the temperature range from 320−240 K. The two black lines, which were each obtained by a linear least-squares fit to the points between 320° and 280° in each Arrhenius plot, accentuate the calculated deviation from linearity at low temperatures.

The rate constant computed for rearrangement of **2a** at 260 K corresponds to a time for half reaction of about two months. However, the C-5 methyl group makes the rearrangement of **2c** to **1f** exothermic, and the exothermicity of this reaction is calculated to make the barrier to reaction lower in **2c** than in **2a** by a little over 2 kcal/mol. The lower barrier height makes the predicted half time for the rearrangement of **2c** less than half a day at 260 K and less than a week at 240 K. Therefore, a kinetic study of the rate of rearrangement of **2c** at temperatures as low as 240 K should, at least in principle, be feasible. An Arrhenius plot of carefully measured rate constants between 240 and 320 K is predicted to show a detectable amount of curvature, due to the calculated 25% decrease in E_a from 20.1 kcal/mol at 320 K to 16.0 kcal/mol at 240 K.

The degenerate nature of the rearrangement of **2a** makes its rate unmeasurable, but Roth did measure the rate of rearrangement of **2b** to **2e** over a temperature range from 343 to 363 K.[10] He obtained $E_a = 24.3 \pm 0.5$ kcal/mol and log $A = 12.1$ for this reaction. The calculated activation parameters for rearrangement of **2b** to **1e** at 353 K are $E_a = 24.5$ kcal/mol and

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(19) The greater decrease with temperature of the E_a for tunneling by protium than by deuterium means that linear extrapolation of an Arrhenius plot of k_H/k_D from high temperatures to low temperatures will tend to significantly underestimate the size of the KIE at low temperatures. For example, our unpublished MPW1K/6-31+G(d,p) calculations on the [1,5]sigmatropic rearrangements of Z-1,3-pentadiene-1,1-d_2 (**1b**) and Z-1,3-pentadiene-5,5,5-d_3 (**1c**), the reactions used by Roth and König to define k_H/k_D,[1] find a KIE for this reaction of 4.9−4.3 over the temperature range from 453 to 484 K. The average value of 4.6 is a little lower than the average value of 5.1 that was measured over this temperature range by Roth and König. However, extrapolated linearly, their Arrhenius expression for k_H/k_D gives a KIE of 12.2 at room temperature,[1] whereas our CVT + SCT calculations predict a KIE of 36.2 at 298 K. The reason for this factor of three difference between their extrapolated and our calculated KIE at 298 K is that E_a for tunneling by protium decreases faster with temperature than E_a for tunneling by deuterium, so that k_H decreases less rapidly with temperature than k_D. Put another way, the greater curvature of the Arrhenius plot of k_H than that of k_D makes the calculated KIE at room temperature much larger than the KIE obtained by assuming that the Arrhenius plot continues to remain linear from 453 to 298 K.

(20) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: New York, 1980; pp 21−26.

log $A = 12.7$, in excellent agreement with the values measured by Roth around this temperature.

As shown in Table 2, the calculated activation parameters for rearrangement of **2c** and **2d** are also in good agreement with the experimental values, measured by McLean and co-workers.[11] Consequently, as shown in Table 1, the ratios of the calculated rate constants for these two reactions at different temperatures also agree well with the KIEs that were measured at these temperatures.

Both the calculated and measured KIEs are strongly temperature-dependent and decrease by 60−70% over the 40° interval between 280 and 320 K. This large decrease must reside in the large differences between the activation energies for the rearrangements of **2c** and **2d**. Table 1 shows that tunneling through, rather than passage over, the reaction barrier dominates all the rate constants in this temperature range. Therefore, the large isotope effects on both the activation energies and pre-exponential factors for the rearrangements of **2a**/**2b** and **2c**/**2d** are due to differences between the activation parameters for tunneling by hydrogen and deuterium in these reactions.[21]

The factor of 2 greater mass of deuterium means that, at equal energies, $E^{\ddagger}$, below the top of the barrier, the probability of tunneling is much less for deuterium than that for hydrogen.[20,22] Tunneling only becomes as probable for deuterium as for hydrogen if the effective height and width of the barrier through which tunneling must occur are significantly smaller for deuterium than those for hydrogen. Because the effective height, $E^{\ddagger}$, and with it the effective width of the barrier decrease as the energy at which tunneling occurs increases, tunneling by deuterium occurs closer to the top of the barrier than tunneling by hydrogen. Consequently, as illustrated schematically in Figure 3, at 300 K tunneling by deuterium in **2d** requires more thermal activation than tunneling by hydrogen in **2c**. This is the main reason that the E_a values in Table 2 are higher for **2d** than those for **2c** and the values for **2b** are higher than those for **2a**.[23]

Interestingly, at the average energy at which thermally activated tunneling takes place in each compound at 280 K, comparison of the pre-exponential factors for tunneling of the deuteriated and undeuteriated compounds (see Tables 1−4 of the Supporting Information) shows that the tunneling probabilities for the deuteriated compounds (**2b** and **2d**) are actually about 10 times larger than those for the undeuteriated compounds (**2a** and **2c**). Apparently, the lower effective barrier heights and widths for tunneling by deuterium more than overcome the effect of the larger mass of deuterium on the probability of tunneling.

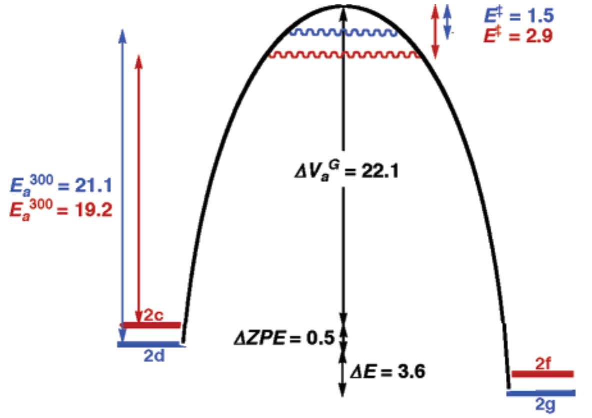

Figure 3. Schematic depiction of thermally activated tunneling in the rearrangements of **2c** and **2d** at 300 K. All the energy differences are given in kcal/mol. Note that the E_a values shown for tunneling are slightly smaller than the overall E_a values given in Table 2, because the latter are weighted averages that include contributions from molecules that pass over the top of the barrier.

Although at first counterintuitive, a higher *A* factor for tunneling by deuterium than by hydrogen actually makes sense. Consider the limit where tunneling by deuterium occurs so close to the top of the barrier in Figure 3 that the effective barrier height ($E^{\ddagger}$) and barrier width both approach zero. Then the pre-exponential factor for tunneling would approach that for passage of deuterium over the top of the barrier, which certainly would be higher than that for tunneling of hydrogen through the barrier.

In general, thermally activated tunneling by deuterium should have both a higher E_a and a higher *A* value than thermally activated tunneling by hydrogen.[22] Consequently, as the temperature increases, the rate constants for tunneling by hydrogen and by deuterium approach each other, and the KIE at high temperatures may be quite small. For example, over the 40° temperature range from 260 to 300 K, the ratios of k(**2a**)/k(**2b**) and k(**2c**)/k(**2d**) are each calculated to drop by about a factor of 2, from 11.8 to 5.50 and from 11.2 to 5.72, respectively.

As shown in Table 1, all four of these [1,5]sigmatropic reactions are still dominated by tunneling at 300 K. Therefore, these reactions provide further examples that illustrate that a modest KIE (e.g., $k_H/k_D = 5.5$) for a reaction at room temperature cannot be taken as evidence that tunneling in that reaction is unimportant.[24]

The computational results reported in Table 2 indicate that measuring the temperature dependence of the KIEs, rather than the size of the KIEs at just one temperature, is a much better probe of whether tunneling by hydrogen plays a major role in a reaction around that temperature.[25] If tunneling is unimportant, the difference between the E_a values for the protio and deuterio compounds will largely be due to the difference between the hydrogen and deuterium zero-point energies (ZPE) for the

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(21) In contrast to the greater than a factor of two overall decrease in the KIEs predicted for these reactions between 260 and 320 K, the KIEs that are calculated for passage *over* the barrier decrease by only about 15%, from 2.59 at 260 K to 2.22 at 320 K for the rearrangement of **2a**/**2b** and from 2.89 to 2.40 for rearrangement of **2c**/**2d**. The small temperature dependence in these over-the-barrier KIEs is because, as shown in Figure 3, the difference between the E_a values for passage of the deuterated and undeuterated cyclopentadienes over the barrier is equal to ΔZPE, which is computed to be only 0.5 kcal/mol.

(22) If tunneling involved a single vibration, H would always tunnel faster than D. However, because tunneling in most molecules is multidimensional, it is possible for D to tunnel faster than H, especially when the contribution of tunneling to the reaction rate is modest. For examples of D tunneling faster than H, see: (a) Garrett, B. C.; Truhlar, D. G. *J. Chem. Phys.* **1980**, *72*, 3460. (b) Truong, T. N.; McCammon, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 7504. (c) Storer, J. W.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 10426. (d) Corchado, J. C.; Espinosa-Garcia, J. *J. Chem. Phys.* **1996**, *105*, 3160. (e) Villa, J.; Gonzalez-Lafont, A.; Lluch, J. M. *J. Phys. Chem.* **1996**, *100*, 19389. (f) Alhambra, C.; Gao, J.; Corchado, J. C.; Villa, J.; Truhlar, D. G. *J. Am. Chem. Soc.* **1999**, *121*, 2253. (g) Cui, Q.; Karplus, M. *J. Am. Chem. Soc.* **2002**, *124*, 3093.

(23) As shown in Figure 3, the 0.5 kcal/mol difference between H and D in the amount of zero-point energy in the reactant that is lost in the TS contributes about 25% of the 1.9 kcal/mol difference in E_a values at 300 K.[21]

(24) For some previous examples, see: (a) Garrett, B. C.; Truhlar, D. G.; Wagner, A. F.; Dunning, T. H., Jr. *J. Chem. Phys.* **1983**, *78*, 4400. (b) Garrett, B. C.; Truhlar, D. G.; Schatz, G. C. *J. Am. Chem. Soc.* **1986**, *108*, 2876. (c) Garcia-Viloca, M.; Alhambra, C.; Truhlar, D. G.; Gao, J. *J. Comput. Chem.* **2003**, *24*, 177. (d) Garcia-Viloca, M.; Truhlar, D. G.; Gao, J. *Biochemistry* **2003**, *42*, 13558.

(25) See, for example: Kohen, A. In *Isotope Effects in Chemistry and Biology*; Kohen, A., Limbach, H.-H., Eds.; Taylor and Francis: Boca Raton, FL, 2006; pp 753−757 and references therein.

vibrational mode in the reactant that becomes the reaction coordinate in the transition structure (TS). If a C−H stretching mode is lost in the TS, values on the order of $\Delta E_a \approx \Delta \text{ZPE} \approx (3000\ \text{cm}^{-1} - 2100\ \text{cm}^{-1})/2 = 450\ \text{cm}^{-1} = 1.3$ kcal/mol can be expected, provided that other isotopically dependent frequencies do not also change significantly on passing from the reactant to the transition state.[26]

On the other hand, as shown by the computational results for **2a**−**d** in Table 2, the difference between the activation enthalpies for thermally activated tunneling by hydrogen and by deuterium can easily exceed 2 kcal/mol. In fact, the size of the difference of $\Delta E_a = 2.5 \pm 0.3$ kcal/mol, measured by McLean and co-workers,[11] between the 1,5-shift of hydrogen in **2c** and of deuterium in **2d** is about twice as large as the maximum value of $\Delta E_a = 1.3$ kcal/mol expected from ΔZPE for C−H and C−D stretching.[26] Consequently, the observed value of $\Delta E_a = 2.5 \pm 0.3$ kcal/mol provides strong *experimental* evidence for the importance of tunneling in the 1,5-hydrogen shift in 5-methyl-1,3-cyclopentadiene.

Conclusions

Our CVT + SCT calculations find that thermally activated tunneling through, rather than passage over, the reaction barrier is the dominant mode of reaction in the [1,5]sigmatropic shifts in both undeuteriated and deuteriated cyclopentadiene (**2a**/**b**) and its 5-methyl derivative (**2c**/**d**). In good agreement with the measurements of McLean and co-workers,[11] our calculations find that, at around 300 K, E_a is a little more than 2 kcal/mol higher, and A is about a factor of 10 larger for the 1,5-deuterium shift in **2d** than for the 1,5-hydrogen shift in **2c**. These computational results indicate that, in general, highly temperature-dependent KIEs, such as those found by McLean and co-workers for the rearrangements of **2c** and **2d**,[11] provide prima facie experimental evidence for the importance of tunneling.

Our calculations also predict that confirmatory experimental evidence for tunneling in **2c** should be found in the curvature around 240−260 K of the Arrhenius plot for its rearrangement to **2f**. The rate of rearrangement of **2c**, even at 240 K, is calculated to be fast enough to make rate measurements at this temperature feasible.

Although we have used calculations to investigate the role of tunneling in the rearrangements of **2a**−**d**, we believe that $\Delta E_a = 2.5 \pm 0.3$ kcal/mol, measured between the 1,5-shift of hydrogen in **2c** and of deuterium in **2d**,[11] provides strong experimental evidence that tunneling is involved in the 1,5-hydrogen shift in **2c**. In addition, our calculations predict that a purely experimental test of this conclusion should be possible. Thus, we are confident that the effects of tunneling, computed by us, for the rearrangement of **2c** are not "relegated to the virtual world of calculation."[5]

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Supporting Information Available: Tables of calculated CVT rate constants and activation parameters, CVT + SCT rate constants and activation parameters for passage over and tunneling through the barrier to [1,5]sigmatropic shifts in **2a**−**d**, Cartesian coordinates and absolute energies for **2a** and **2c** and for the transition structures for 1,5-hydrogen shifts in these hydrocarbons, and the complete list of authors for refs 17 and 18. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) The value of ΔZPE = 0.5 kcal/mol that is computed for the 1,5-hydrogen shifts in cyclopentadienes **2a**−**d** is considerably smaller than 1.3 kcal/mol, because in these rearrangements the vibrational mode that becomes the reaction coordinate in the TS is closer to being a C−H/C−D bend than a C−H/C−D stretch.