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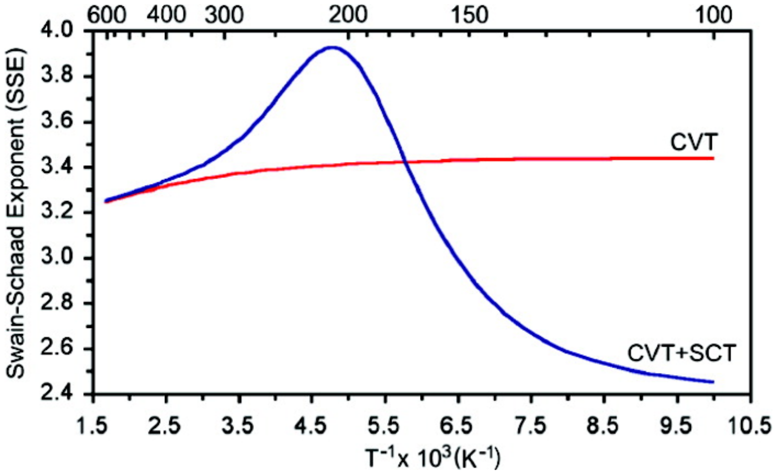
J. Am. Chem. Soc., **2007**, 129 (51), 16115-16118 • DOI: 10.1021/ja076132a



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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ARTICLES

Calculations of the Effect of Tunneling on the Swain−Schaad Exponents (SSEs) for the 1,5-Hydrogen Shift in 5-Methyl-1,3-cyclopentadiene. Can SSEs Be Used to Diagnose the Occurrence of Tunneling?

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Abstract: MPW1K density functional calculations, carried out with the 6-31+G(d,p) basis set, have been combined with canonical variational transition state theory (CVT) and small-curvature tunneling (SCT) corrections in order to compute the primary kinetic isotope effects for rearrangement of 5-methyl-1,3-cyclopentadiene (**1**) to 1-methyl-1,3-cyclopentadiene (**2**). The Swain-Schaad exponents, $SSE = \ln(k_H/k_T)/\ln(k_D/k_T)$, for this reaction have been computed over the temperature range 100−600 K. Tunneling results in both large positive and large negative deviations from the value of $SSE = 3.26$, expected from consideration of only the effect of the isotopic mass on passage over the reaction barrier. In the rearrangement of **1** to **2**, $SSE \approx 3.26$, not only at temperatures >400 K, where tunneling is relatively unimportant, but also around 170 K, where tunneling by both H and D is the dominant mode of reaction. Thus, from an experimental finding that $SSE \approx 3.26$ at a single temperature, it cannot be rigorously concluded that tunneling is unimportant. Measurement of SSEs over a broad temperature range is advisable; but measurement of the temperature dependence of just k_H/k_D can be used to establish more unequivocally whether tunneling is important, without the necessity of measuring k_T.

Introduction

Kinetic isotope effects (KIEs) have long been a tool for investigating the mechanisms of hydrogen transfer reactions.[1] The ratios of the natural logarithms of the rate constants for H, D, and T transfer have become known as the Swain-Schaad exponents (*SSE*s).[2] Assuming that KIEs are due only to the effects of isotope mass on the zero-point energies (ZPEs) for C−H stretching vibrations, Swain and Schaad derived,

$$\begin{aligned} SSE &= \ln(k_H/k_T)/\ln(k_D/k_T) \\ &= (1 - 1/\sqrt{3})/(1/\sqrt{2} - 1/\sqrt{3}) = 3.26 \end{aligned} \tag{1}$$

or, alternatively,

$$\begin{aligned} SSE' &= \ln(k_H/k_T)/\ln(k_H/k_D) \\ &= SSE/(SSE - 1) = 1.44 \end{aligned} \tag{2}$$

Deviations of measured SSE′ from 3.26 (or of SSEs from 1.44) have been used as an indication of the occurrence of tunneling in hydrogen transfer reactions, particularly in reactions catalyzed by enzymes.[3−6] Because of its lighter mass, hydrogen tunnels more efficiently than deuterium or tritium.[7] Therefore, as the reaction temperature is lowered, k_H is expected to decrease less rapidly than k_D or k_T.[3,4] Consequently, an increase in the SSE with decreasing temperature might be expected to be observed for reactions in which tunneling is important.

However, when tunneling is not vibrationally activated, consideration of the one-dimensional tunneling probabilities of H, D, and T through a square[5c] or parabolic barrier leads to[8]

$$SSE = (\sqrt{3} - 1)/(\sqrt{3} - \sqrt{2}) = 2.30 \tag{3}$$

Therefore, as the reaction temperature is lowered and tunneling without thermal activation becomes more important, eq 3 predicts that the SSE should be significantly less, not greater, than 3.26.

Calculations on proton exchange in formic acid dimer, a reaction in which tunneling plays a very important role, find

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(1) See, for example, the excellent reviews in *Isotope Effects in Chemistry and Biology*; Kohen, A., Limbach, H.-H., Eds.; Taylor and Francis: Boca Raton, FL, 2006.

(2) Swain, C. G.; Stivers, E. C.; Reuwer, J. F.; Schaad, L. J. *J. Am. Chem. Soc.* **1958**, *80*, 5885.

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(5) For discussions about the use of the sizes of SSEs for drawing conclusions about tunneling see: (a) Huskey, W. P. *J. Phys. Org. Chem.* **1991**, *4*, 361. (b) Kim, Y.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 3093. (c) Cui, Q.; Karplus, M. *J. Am. Chem. Soc.* **2002**, *124*, 3093.

(6) The use of SSEs for hydrogens not being transferred (i.e. from measurements of secondary kinetic isotope effects) as an indication of tunneling has been shown to be problematical. (a) Stern, M.; Vogel, P. C. *J. Am. Chem. Soc.* **1971**, *93*, 4664. (b) Hirschi, J.; Singleton, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 3294−3295.

(7) Bell, R. P. *The Tunneling Effect in Chemistry*; Chapman and Hall: New York, 1980.

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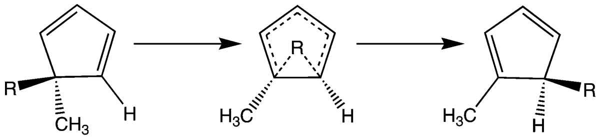
that the computed *SSE*s do, in fact, decrease smoothly from 2.6 at 400 K to 2.1 at 100 K.[9] However, the finding that at 400 K the SSE is much closer to 2.30 than to 3.26 is a strong indication that, even at this temperature, the reaction is dominated by tunneling of all three isotopes of hydrogen.

What is the temperature dependence of the SSE when a hydrogen-transfer reaction proceeds by passage over the barrier at high temperatures but by passage through the barrier at low temperatures? Does the SSE decrease smoothly from a value near 3.26 at high temperatures to a value close to 2.30 at low temperatures,[8] or does the SSE first increase[3,4] and then decrease as the temperature is lowered?[5c]

In order to address this question, we have computed the rate constants for the rearrangements of 5-methyl-1,3-cyclopentadiene (**1a**) and its 5-D (**1b**) and 5-T (**1c**) isotopomers to the respective 1-methyl-1,3-cyclopentadienes **2a**−**c** over the temperature range 100−600 K. We have previously reported the results of our calculations on the rearrangements of **1a** and **1a**-d_5 in the temperature range 280−320 K,[10] where the rate of reaction has been measured experimentally.[11] The excellent agreement of our calculated activation energies with the experimental values over this temperature range for the 1,5-shifts of H and D in **1a** and **1a**-d_5, respectively, suggests that the rate constants for rearrangements of **1a**−**c**, computed over a much wider temperature range, should also be quite accurate. In this paper we report the results of our calculations on the temperature dependence of the SSE for the rearrangement of **1** to **2**.



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

2a, R = H
b, R = D
c, R = T

Computational Methodology

As in our previous study of the rearrangement of **1a** and **1a**-d_5 to **2a** and **2a**-d_5, respectively, Truhlar's MPW1K functional[12] and the 6-31+G(d,p) basis[13] set were employed in our calculations. 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.[15] Direct dynamics calculations were carried out with GAUSSRATE[16] as the interface between Gaussian03[17] and POLYRATE.[18]

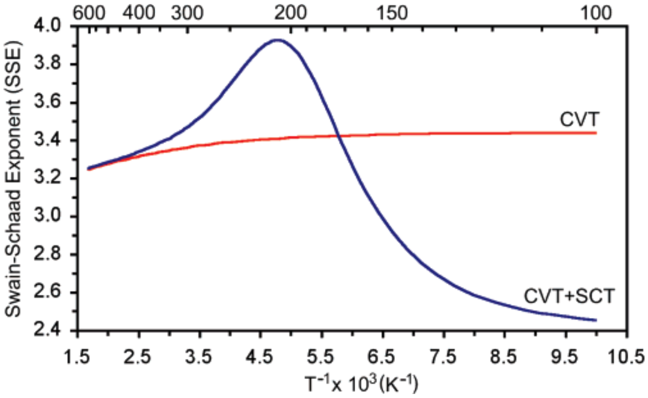


Figure 1. Plot of the calculated Swain−Schaad exponents (SSE) for the rearrangement of **1** to **2** versus 1/*T*.

Results and Discussion

The Swain−Schaad exponents for the rearrangement of **1a**−**c** to **2a**−**c** in the temperature range of 100−600 K have been computed from the definition in the first line of eq 1, using the rate constants obtained from both CVT and CVT + SCT calculations. The results are presented graphically in Figure 1.

Using the CVT rate constants, *SSE* is nearly constant over this 500° temperature range, increasing from 3.25 at 600 K to 3.44 at 100 K. Particularly in the high-temperature range, *SSE* is very close to the value of $SSE = 3.26$ predicted from the isotopic masses by eq 1.[2] As noted in the introduction, eq 1 is based on the assumption that the differences between k_H, k_D, and k_T are due entirely to differences between the zero-point energies for the stretching vibrations of these three isotopes in **1a**−**c**.

As shown in Figure 1, when small-curvature tunneling (SCT) is included, *SSE* varies with temperature in a much more complicated fashion. At high temperatures the CVT + SCT curve approaches the CVT curve asymptotically, as more and more molecules react either by passage over the barrier or by vibrationally assisted tunneling very close to the top of the barrier. In contrast, at 100 K, where most of the molecules react by passage through the barrier, with little vibrational activation, the CVT + SCT curve shows the greatest deviation from the CVT curve. At low temperatures the CVT + SCT curve approaches asymptotically a value around 2.3, as predicted by eq 3, which is based on the assumption that the differences between k_H, k_D, and k_T are due entirely to differences between the tunneling probabilities of these three isotopes.[5c,8]

What is not explained by eq 1 or by eq 3 is why *SSE* increases with decreasing temperature, until it reaches a maximum just above 200 K and why *SSE* then decreases until it asymptotically approaches the limiting, low-temperature value of $SSE = 2.3$. In order to understand the temperature dependence of *SSE* for the rearrangement of **1a**−**c** to **2a**−**c**, it is advantageous to rewrite the definition of *SSE* in eq 1 in terms of the Arrhenius expressions for the three rate constants. The result is eq 4.

$$SSE = [\ln(A_H/A_T) - (E_a^{\,H} - E_a^{\,T})/RT]/ [\ln(A_D/A_T) - (E_a^{\,D} - E_a^{\,T})/RT] \quad (4)$$

At very low temperatures, tunneling becomes temperature independent; thus $E_a^{\,H} = E_a^{\,D} = E_a^{\,T} \approx 0$. Equation 4 then reduces to

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$$SSE \approx \ln(A_H/A_T)/\ \ln(A_D/A_T) \qquad (5)$$

which is the ratio of the mass-dependent tunneling probabilities, given by eq 3.[5c,8] However, at high temperatures the differences between the E_a's dominate eq 4, which becomes

$$SSE \approx (E_a^{\ T} - E_a^{\ H})/(E_a^{\ T} - E_a^{\ D}) \qquad (6)$$

If the differences between the activation energies for reaction are equal to the differences between the zero-point energies of H, D, and T stretching vibrations in **1a**−**c**, then eq 1 is obtained.

As the temperature is reduced and tunneling begins to affect the high-temperature rate constants, the effects of tunneling on reducing the energies in eq 6 must be considered. The smaller mass of hydrogen allows it to tunnel more effectively than deuterium or tritium.[7] Consequently, as the temperature is lowered, $E_a^{\ H}$ begins to decrease first.[3,4] This decrease in $E_a^{\ H}$ is responsible for the initial increase of *SSE* with decreasing temperature, which is shown in Figure 1.

This increase in *SSE* continues until deuterium begins to tunnel. The resulting decrease in $E_a^{\ D}$ in eq 6 causes the rate of increase of *SSE* to slow. When *SSE* reaches a maximum, $dSSE/dT^{-1} = 0$. It is thus easy to show that the maximum occurs when

$$(dE_a^{\ H}/dT^{-1})/(dE_a^{\ D}/dT^{-1}) = (E_a^{\ T} - E_a^{\ H})/\ (E_a^{\ T} - E_a^{\ D}) \qquad (7)$$

after which *SSE* begins to decrease. Finally, as tritium begins to tunnel, $E_a^{\ T}$ decreases, until the mass-dependent tunneling probabilities dominate eq 4, which then reduces to eq 5.

The temperature dependence of the CVT + SCT rate constants, k_H, k_D, and k_T, is shown graphically in the three Arrhenius plots in Figure 2. As previously discussed,[10] in the rearrangement of **1a** to **2a**, curvature of the Arrhenius plot for k_H, caused by the decrease in $E_a^{\ H}$ as tunneling increases, becomes noticeable below 300 K. As shown in Figure 1, this is the temperature region in which the increase in *SSE* with decreasing temperature is largest.

The onset of curvature in the Arrhenius plot for k_D in Figure 2, shows that, at a little above 200 K, tunneling by deuterium begins to result in a decrease in $E_a^{\ D}$. This decrease produces the maximum in the plot of *SSE* versus $1/T$ in Figure 1 around 200 K.[19]

Figure 2 also reveals that around 160 K tunneling by tritium begins to result in a decrease in $E_a^{\ T}$. This decrease results in the decrease in the downward slope of the plot of *SSE* versus $1/T$ in Figure 1 around this temperature.

Finally, Figure 2 shows that at very low temperatures the slopes of the Arrhenius plots for all three hydrogen isotopes asymptotically approach the value of zero that results when tunneling occurs only from the lowest vibrational levels of **1a**−**c**. As vibrationally assisted tunneling grows less and less important, the plot of *SSE* versus $1/T$ in Figure 1 approaches the value of $SSE = 2.30$ that is expected on the sole basis of the effect of mass on the tunneling probabilities.[5c,8]

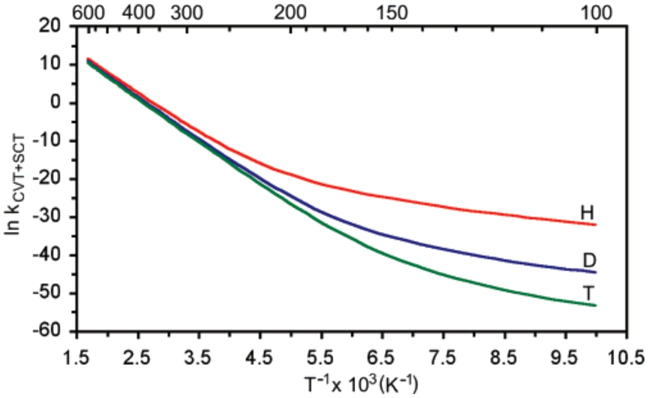

Figure 2. Arrhenius plots of k_H, k_D, and k_T for, respectively, the rearrangements of **1a**−**c** to **2a**−**c**.

Conclusions Regarding the Effects of Tunneling on SSEs

As already noted, the excellent agreement of our calculated activation energies[10] with the experimental values[11] for the 1,5-shifts of H and D in **1a** and **1a**-d_5, suggests that the plot of *SSE* versus $1/T$ in Figure 1 is probably similar to the plot that would be obtained if the rate constants for the rearrangements of **1a**−**c** could actually be measured from 100−600 K. Therefore, it is reasonable to ask, what does the plot in Figure 1 indicate, in general, about the use of experimentally measured *SSE*s as indicators of the occurrence of tunneling in chemical reactions?

First, large deviations, *both positive and negative*, from $SSE = 3.26$ are indicative of tunneling. The effect of tunneling on $E_a^{\ H}$ is responsible for the positive deviation in Figure 1, and the effect of tunneling on $E_a^{\ D}$ is largely responsible for the negative deviation seen at lower temperatures. Approach of *SSE* toward the limiting value of 2.30 at very low temperatures indicates that vibrationally unassisted tunneling is the dominant mode of reaction for all three isotopomers.

Second, a value of $SSE \approx 3.26$ does not rigorously exclude the occurrence of tunneling. *SSE* for the rearrangement of **1** to **2** has a value of about this size, not only at high temperatures, where tunneling is relatively unimportant, but also around 170 K, where the curved Arrhenius plots for H and D in Figure 2 show that tunneling plays an important role in the reactions of both **1a** and **1b**.

Third, for investigating whether tunneling is important in a chemical reaction, measurement of *SSE* over as wide a temperature range as possible is obviously much better than a measurement of *SSE* at a single temperature. For example, measurements of *SSE* for the rearrangement of **1a**−**c** in the temperature range from 600−300 K would show that *SSE* only increases by 7%, from 3.25 to 3.49, over this 300° temperature range, thus indicating that tunneling plays a relatively minor role in this temperature range. However, as shown in Figure 1, measurements of rate constants around 170 K, where *SSE* also has a value close to 3.26, would reveal a much stronger dependence of *SSE* on temperature, thus indicating a major role for tunneling in the rearrangement of **1** around this temperature.

Is measurement of the temperature dependence of *SSE* for a reaction the best way to investigate whether tunneling is important in that reaction over a particular temperature range? We think not.

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(19) The onset of curvature around 200 K in the Arrhenius plot of k_D for rearrangement of **1b** also produces a point of inflection in the Arrhenius plot of k_H/k_D at about this temperature, as the slope of the latter plot goes from being dominated by tunneling by hydrogen above 200 K to being dominated by tunneling by deuterium below 200 K. The Arrhenius plot for the H/D KIE for the rearrangement of **1a** and **1b** is available in the Supporting Information for this manuscript.

For example, we have previously pointed out that in the rearrangements of **1a** and **1a**-d_5 to **2a** and **2a**-d_5, respectively, the large temperature dependence of k_H/k_D around 300 K provides *prima facie* evidence for the importance of tunneling in this reaction.[10,20] A 60% increase in k_H/k_D is calculated between 320 and 280 K,[10] and a 70% increase is found in the experimental values, using the Arrhenius plots for k_H and k_D.[11]

By comparison, the calculated 4% increase in the *SSE* for the rearrangements of **1a**−**c**, from $SSE = 3.40$ at 320 K to $SSE = 3.53$ at 280 K, is much more modest. In addition, even at 280 K, the lowest temperature at which k_H could be conveniently measured,[11] the deviation of *SSE* from the value of $SSE = 3.26$ (expected in the absence of tunneling[2]) is only 8%. The rate constants for the rearrangements of **1a**−**c** would have to be measured with very high accuracy in order to have complete confidence that a value of $SSE = 3.53$ really was indicative of tunneling and was not just due to experimental errors in the measured rate constants.

An experimental determination of the SSE for the rearrangements of **1a**−**c** to **2a**−**c** would, of course, require very accurate measurements of not only the rate constants for the 1,5-shifts of H and D in **1a** and **b** but also of T in **1c**. For purely practical reasons, measurement of only k_H in **1a** and k_D in **1b** would, of course, be preferable to having also to synthesize **1c** and to measure k_T for its rearrangement to **2c**.[21] Preparing **1c** and measuring k_T for its rearrangement to **2c** would be particularly onerous, since the values of *SSE* thus obtained would provide less compelling evidence for the importance of tunneling than just measuring the temperature dependence of k_H/k_D.

Acknowledgment. We thank the National Science and Robert A. Welch Foundations for supporting this research. Some of the calculations reported here were performed on computers purchased with funds provided by the National Science Foundation under Grant CHE-0342824.

Supporting Information Available: Table of CVT and CVT + SCT rate constants for the rearrangements of **1a**−**c** to **2a**−**c** over the temperature range 100−600 K, the Arrhenius plot of k_H/k_D for **1a** and **1b**, 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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(20) For a review of the use of the temperature dependence of k_H/k_D primary KIEs for diagnosing the occurrence of tunneling, see Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401.

(21) The value of k_D for the rearrangement of **1** was obtained by measuring the rate of rearrangement of **1**-d_5, which was prepared by methylation of cyclopentadienyl anion-d_5.[11] Since tritium is radioactive, a comparable experiment to measure k_T for the rearrangement of **1**-t_5 would not be feasible.