J. Am. Chem. Soc. 1990, 112, 4151-4154

Vibrationally Assisted Tunneling in the [1,5] Sigmatropic Hydrogen Shift in *cis*-1,3-Pentadiene

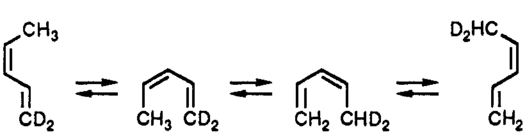
Lek Chantranupong and Timothy A. Wildman*

Contribution from the Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4M1.

Received June 21, 1989

Abstract: The primary kinetic isotope effect on the thermal [1,5] sigmatropic hydrogen shift in *cis*-1,3-pentadiene has been studied. While the preferred conformation of the molecule is s-trans, both semiempirical and ab initio molecular orbital calculations indicate that a gauche conformer, not the planar s-cis, is a local minimum on the potential energy surface. Hydrogen-transfer rate constants have been calculated for this conformer through the use of a simple, two-dimensional quantum mechanical model. Although the rate constant exhibits an Arrhenius temperature dependence in the range of experimental investigation, the magnitude of the isotope effect is strongly indicative of tunneling. In the model, a low-frequency vibrational mode (or modes) promotes the process by allowing the molecule to attain nonequilibrium geometries that are more favorable to hydrogen migration than is the equilibrium structure. For the first time, both the derived activation energy and the kinetic isotope effect are in agreement with experiment. Calculational results demonstrate that vibrationally assisted tunneling dominates the transfer rate at temperatures above 100 K.

Several years ago, Roth and König[1] studied the kinetics of the thermal [1,5] sigmatropic hydrogen shift in *cis*-1,3-pentadiene.



1a **1b** **2b** **2a**

They followed the course of the reaction for 1,1-dideuterio-*cis*-1,3-pentadiene (**1**) and for 5,5,5-trideuterio-*cis*-1,3-pentadiene in the temperature range 458–484 K by ^{1}H NMR spectroscopy. From an analysis of the relative areas of vinyl and methyl resonances as a function of time, they extracted first-order rate constants for H and D transfer which led to an enthalpy of activation, ΔH^*, of 148 kJ·mol^{-1} and an entropy of activation, ΔS^*, of −30 J·mol^{-1}·K^{-1}. The primary kinetic isotope effect on the rate was remarkably large: $k_H/k_D = 5$ at 473 K. Several computational studies of this process have been concerned with the description of a classical transition-state structure while debating the importance of quantum-mechanical tunneling.[2-7] None have reproduced so large an isotope effect.

Because the Arrhenius plots for hydrogen transfer show no indication of curvature (see Figure 1), it might seem that this reaction can be described in terms of a conventional thermally activated process. Calculated activation enthalpies are usually given relative to the stable s-trans conformer **a**, although it is apparently an s-cis-like conformer **b** that leads to reaction. There is no spectroscopic evidence for an appreciable population of any conformer except conformer **a** below 473 K.[8] MINDO/3 calculations yield a rather high value for ΔH^*. Subsequent ab initio calculations with the 3-21G basis produced similar results.[7] However, the difference between post-Hartree–Fock energies for the s-trans conformer and the C_s transition state was found to be in good agreement with the experimental ΔH^*,[5] which might be taken as evidence that the reaction is conventional. More recently, it has been argued that the classical barrier height cannot be calculated with sufficient accuracy to support this conclusion.[6] Calculations of the kinetic isotope effect, based on the method of periodic orbits[6] or on Bigeleisen's equation,[7,9] gave values of k_H/k_D that were about one-half of those observed, which suggests that tunneling is important. A classical treatment seems incapable of producing the experimental isotope effect.

Dewar et al. have suggested that the discrepancies between the experimental and computational results could be explained by quantum-mechanical tunneling through the reaction barrier, but tunneling between the vibrational ground states of the reactant and product would be highly improbable given the significant difference in equilibrium geometry between **1b** and **2b**.[6] Direct conversion between the vibrational ground states of **1a** and **2a** is even less probable. Therefore, some modification of the basic notion is required, namely, consideration of molecular motions that may assist tunneling.

Ground-state tunneling occurs because the zero-point motion within the vibrational potential allows a small but finite probability that the hydrogen may be found in the classically forbidden region where the vibrational potential energy exceeds the kinetic energy. If the tails of the ground-state vibrational wave functions for hydrogen motion in the reactant and product geometries overlap, it is possible for the migrating hydrogen to traverse the classically forbidden region, i.e. the reaction barrier, even if it has insufficient thermal energy. Clearly, this process contributes only to the point at which the difference between reactant and product geometries is so great that for all practical purposes the overlap vanishes. In the same way, tunneling can occur between excited vibrational levels of the CH oscillator that are below the reaction barrier, but in that case the more favorable transfer rate associated with better overlap is balanced by the lower thermal population of the state. In this oversimplified and popular view,[10] transfer is said to occur in one dimension, namely along the coordinate that describes the motion of the migrating atom.

More importantly, the transfer may occur by tunneling while the CH oscillator is in the ground state but a low-frequency oscillator, e.g. a skeletal mode, is in an excited state. Although such a state has a lower thermal population than the ground state,

---

(1) Roth, W. R.; König, J. *Liebigs Ann. Chem.* **1966**, *699*, 24. Roth, W. R. *Chimia* **1966**, *20*, 229.

(2) Kwart, H.; Brechbiel, M. W.; Acheson, R. M.; Ward, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 4671. Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401.

(3) Bingham, R. C.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1972**, *95*, 9107. Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294.

(4) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7185. Hess, B. A., Jr.; Schaad, L. J.; Pancir, J. *J. Am. Chem. Soc.* **1985**, *107*, 149.

(5) Rondan, N. G.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 2159. Kahn, S. D.; Hehre, W. J.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 8291. Jensen, F.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 3139.

(6) Dewar, M. J. S.; Merz, K. M., Jr.; Stewart, J. J. P. *J. Chem. Soc., Chem. Commun.* **1985**, 166. Dewar, M. J. S.; Healy, E. F.; Ruiz, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 2666.

(7) Dormans, G. J. M.; Buck, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 3253. Dormans, G. J. M.; Buck, H. M. *J. Mol. Struct.* **1986**, *136*, 121.

(8) Compton, D. A. C.; George, W. O.; Maddams, W. F. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1311.

(9) Bigeleisen, J.; Wolfsberg, M. *Adv. Chem. Phys.* **1958**, *1*, 15. van Hook, W. A. In *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand: New York, 1970.

(10) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: London, 1980.

0002-7863/90/1512-4151$02.50/0

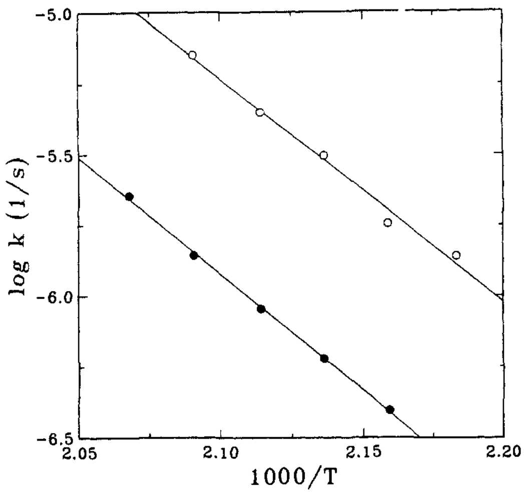


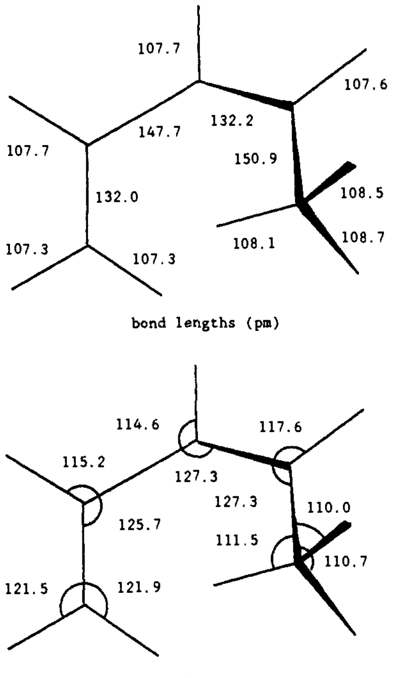
Figure 1. An Arrhenius plot of the hydrogen-transfer rate data from the work of Roth and König (ref 1). Open circles represent H transfer in 1,1-dideuterio-*cis*-1,3-pentadiene. Solid circles represent D transfer in 5,5,5-trideuterio-*cis*-1,3-pentadiene. The lines correspond to least-squares fits.

it may access nonequilibrium geometries that provide a higher transfer probability. The low-frequency mode will enhance the overall transfer rate if the higher transfer probability more than compensates for the lower themal population of the initial state. Dewar and co-workers' phrase "vibrationally assisted tunneling" (VAT) aptly describes the process.[6] Because the mechanism involves two (or more) adiabatically separable motions, namely, the motion of the migrating atom and the motion of the skeleton, the process is said to occur in two (or more) dimensions. A relatively simple model that embodies this idea has been described and applied to a variety of hydrogen-transfer reactions.[11]

Computational Method

Ab initio molecular orbital calculations were performed with Gaussian 86.[12] Semiempirical calculations were performed with the AM1 method, an improved MNDO method,[13] in AMPAC (QCPE 506).[14] Computations were performed to obtain conformational energies and geometries and to help characterize the skeletal vibrations. The process **1a** → **2a** is described as consecutive steps: (i) conformers **1a** and **1b** are in rapid thermal equilibrium, (ii) **1b** undergoes a hydrogen shift to form **2b**, and (iii) **2b** is in rapid equilibrium with the more stable conformer **2a**. The two-dimensional, quantum-mechanical model described in ref 11 was used to describe the second step. In this model, the reactant and product states are described by harmonic CL-stretching potentials (L = H or D) for the bonds broken and formed, and by a single, adiabatically separable, low-frequency motion that promotes the reaction. Exchange of energy between these modes themselves and between these modes and the unspecified molecular vibrations is allowed implicitly. In order to perform the simplest calculation with the fewest input parameters, the transfer was taken to be collinear. The first-order transfer rate constant is calculated from first-order, time-dependent perturbation theory, which is appropriate to the initial rate in the absence of back reaction. The model was parametrized with spectroscopic data[8] and some of the quantum chemical results.

Conformational Equilibrium. The first step in our rate constant calculation is to determine the equilibrium geometry of the reactive conformer and its energy relative to the s-trans conformer. From the energies obtained in previous calculations with the 3-21G basis[4,7] and from



dihedral angles (degrees)

C4C3C2C1	48.3	C5C4C3C2	1.6
HC1C2C3	0.5	HC1C2C3	179.2
HC2C3C4	225.7	HC3C2C1	226.5
HC4C3C2	180.0	HC5C4C3	14.2
HC5C4C3	134.9	HC5C4C3	253.4

Figure 2. The 3-21G optimum geometry for the gauche conformer of *cis*-1,3-pentadiene. The total energy is −192.875 366 au.

the present calculations, the minimum-energy C_s s-trans conformer is about 27 kJ·mol^{-1} more stable than the C_s s-cis conformation. Contrary to earlier reports,[6,7] the C_s s-cis conformation is not stable but corresponds to a relative *maximum* in the rotational potential and a saddle point on the potential energy surface, i.e. there is one negative force constant that corresponds to an imaginary frequency of 202 cm^{-1}. It is therefore inappropriate to select this as the (stable) reactive conformer. Dormans and Buck,[7] who obtained the same total energy (−192.869 668 au) and geometry, found no negative force constants for this structure. Perhaps this discrepancy, and another found by Jensen and Houk,[5] can be attributed to the different methods used to calculate the force constant matrix: finite differences in analytical forces were used by Dormans and Buck but analytical second derivatives were used in the present work.

Complete geometry optimization, initiated with a slight distortion of the s-cis geometry from C_s symmetry, led to a true local minimum corresponding to a gauche conformer of C_1 symmetry. This geometry is given in Figure 2. The principal distortion of the carbon framework is a twist through 48° about the C2C3 bond. The total energy for this structure is −192.875 366 au, i.e. 11 kJ·mol^{-1} above s-trans and 15 kJ·mol^{-1} below s-cis. While the accuracy of the energy difference at this level of approximation may be questionable, the magnitude of the difference is probably reliable. Because $\exp[-(11\ \text{kJ·mol}^{-1})/k_BT]$ is only 0.06 at 473 K, this value is consistent with the fact that no conformers other than s-trans are observed below 473 K.[8] Geometry-optimized AM1[14] calculations also reveal a local minimum corresponding to a twist through 38° about C2C3, in reasonably good agreement with the 3-21G result. However, the energy difference between conformers is only 4.5 kJ·mol^{-1} with AM1, whereby $\exp[-(4.5\ \text{kJ·mol}^{-1})/k_BT]$ is 0.32 at 473 K. This value seems incompatible with experiment. Arguably, these energy differences are equivalent within the expected accuracy of the methods, but given that the gauche conformer has not been observed, the 3-21G result is preferred.

In the present treatment, the stable s-trans and gauche conformers are of key importance. It is unnecessary (and undesirable) to attach special significance to any structure that is unstable or metastable, i.e. a saddle point. This viewpoint contrasts with previous studies of this reaction, which have focused attention on the structure and energy of a classical transition state. For the rate-constant calculations, the reactive gauche conformer **b** is assumed to be in constant thermal equilibrium with the

---

(11) Siebrand, W.; Wildman, T. A.; Zgierski, M. Z. *J. Am. Chem. Soc.* **1984**, *106*, 4083. Siebrand, W.; Wildman, T. A.; Zgierski, M. Z. *J. Am. Chem. Soc.* **1984**, *106*, 4089. Doba, T.; Ingold, K. U.; Siebrand, W.; Wildman, T. A. *J. Phys. Chem.* **1984**, *88*, 3165. Smedarchina, Z.; Siebrand, W.; Wildman, T. A. *Chem. Phys. Lett.* **1988**, *143*, 395.

(12) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *Gaussian 86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, 1984.

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

(14) Dewar Research Group; Stewart, J. J. P. *QCPE Bull.* **1986**, *6*, 24.

Table I Calculated Harmonic Vibrational Frequencies (cm^{-1}) for the Gauche Conformer of *cis*-1,3-Pentadiene

mode	3-21G	AM1		
			1,1-diD	5,5,5-triD
1	3398	3214	3159	3214
2	3329	3178	3148	3178
3	3324	3158	3142	3157
4	3305	3145	3138	3144
5	3296	3141	3049	3138
6	3287	3137	3038	2253
7	3228	3049	2353	2246
8	3186	3038	2346	2238
9	1859	1899	1896	1898
10	1840	1848	1819	1848
11	1666	1483	1477	1476
12	1662	1436	1421	1408
13	1616	1399	1389	1318
14	1584	1398	1381	1283
15	1572	1380	1311	1224
16	1473	1313	1279	1159
17	1411	1280	1201	1059
18	1247	1196	1151	1045
19	1215	1156	1082	1024
20	1200	1082	1058	1005
21	1163	1057	1012	1000
22	1144	1052	975	986
23	1117	1016	945	970
24	1014	983	871	885
25	922	946	833	862
26	854	800	778	739
27	796	720	660	672
28	647	593	504	578
29	484	427	392	408
30	354	318	298	306
31	252	240	230	216
32	190	167	161	144
33	112	94	88	79

Table II Parameter Values for the Calculation of $\tilde{k}_L(T)$

	L = H	L = D
CL stretching		
frequency, cm^{-1}	2970	2100
reduced mass, amu	1.00	2.00
bond length, pm	109	109
promoting mode		
frequency, cm^{-1}	390	390
reduced mass, amu	1.95	1.95
eq'm separation, pm	383	383
coupling strength, ζ	1.625	

more stable but unreactive s-trans conformer **a**. The calculated rate constants are given by

$$k_L(T) = \tilde{k}_L(T) \exp(-\Delta E/k_B T) \qquad (1)$$

where $\tilde{k}_L(T)$ is the quantum-mechanical tunneling rate constant for the gauche conformer, ΔE is the energy of the gauche conformer relative to s-trans, k_B is Boltzmann's constant, and T is temperature.

Parameters for the Calculation of $\tilde{k}_L(T)$. Our aim in the selection of parameter values to describe the process **1b** → **2b** is to avoid arbitrary numbers insofar as possible and to use values derived from experiment or quantum chemical calculations. The values are summarized in Table II.

According to our ab initio results for the gauche conformer, the equilibrium separation of the terminal carbon atoms is 331 pm (315 pm from AM1). The hydrogen-transfer distance, which is defined as the distance between the migrating hydrogen and the terminal methylene carbon minus one standard CH bond length, is 165 pm (152 pm from AM1).

Compton et al. have assigned the fundamental of the antisymmetric methyl stretch to a band at 2970 cm^{-1}.[8] For simplicity, the harmonic frequencies used for the CL-stretching vibration in the rate constant calculations are 2970 cm^{-1} for H and $2970/\sqrt{2} = 2100$ cm^{-1} for D. No attempt was made to incorporate secondary isotope effects, which are probably inconsequential in the present case, nor was anharmonicity included. The reduced masses for these oscillators are 1 and 2 for L = H and D, respectively. Bond lengths are the standard 109 pm.

The promoting mode is more difficult to define. The low-frequency skeletal modes of the (C_s) s-trans conformer have not been characterized[8] and, in any event, would not be appropriate to the gauche conformer. Frequency calculations were performed with the 3-21G basis for the minimum-energy (C_1) gauche conformer. Some results are listed in Table I, along with the AM1 results for comparison. On the whole, the frequencies calculated with the AM1 method were similar to the 3-21G values. The lowest frequency A' mode in C_s symmetry correlates with the third-lowest mode at 252 cm^{-1} (240 cm^{-1} with AM1), for which the reduced mass is 1.95 amu. According to the normal coordinate analyses for the ten lowest modes, this mode results in the largest amplitude modulation for both the hydrogen-transfer distance and the terminal carbon atom separation. This might be chosen as the promoting mode a priori, but that would neglect the contributions of all other motions that modulate the transfer probability. Furthermore, the composition of the normal coordinates in terms of atomic displacements is probably still sensitive to the quality of the basis set at the relatively low level of the present molecular orbital calculations. Because the reduced masses associated with all of the low-frequency modes are comparable (1.34–2.95 amu), the value of the reduced mass was fixed at 1.95 amu and the frequency was varied to reproduce the observed isotope effect. A frequency of 390 cm^{-1} provides reasonable agreement with experiment. The mass and frequency for the promoting mode were not adjusted for different isotopomers. AM1 calculations yielded the frequencies 230 cm^{-1} for the 1,1-dideuterio isotopomer and 216 cm^{-1} for the 5,5,5-trideuterio isotopomer.

For the chosen parameter values, k_H/k_D is 4.8 at 475 K and the derived activation energy is about 94 kJ·mol^{-1}. To illustrate the sensitivity of these quantities to the choice of parameter values, calculations were performed in which the frequency of the promoting mode (Ω), the reduced mass for the promoting mode (M), or the equilibrium separation of the terminal carbon atoms (R_{eq}) was reduced by 10%. If Ω is chosen as 351 cm^{-1}, k_H/k_D is 3.1 and the activation energy is 86 kJ·mol^{-1}. Similar reduction in M to 1.755 amu provides k_H/k_D as 3.8 and the activation energy is 90 kJ·mol^{-1}. If R_{eq} is reduced to 344.7 pm, k_H/k_D is 2.6 and the activation energy is 61 kJ·mol^{-1}. Clearly, the interdependence of these parameters is important. For example, a reduction in Ω can be offset by increasing R_{eq} within reasonable limits. In the present work, we have treated the molecular vibrations in the simplest fashion that will allow VAT. Because R_{eq} is set at the value from the 3-21G calculation and M is taken to represent the reduced masses of the various low-frequency modes, albeit arbitrarily, there is essentially one adjustable parameter, Ω, the value of which must be similar to the calculated frequencies of possible promoting modes.

Discussion

Arrhenius plots of the first-order rate constants obtained by Roth and König[1] appear in Figure 1. While a contribution from ground-state tunneling can lead to significant positive curvature of the Arrhenius plot at low temperatures,[10,11] the data for *cis*-1,3-pentadiene fall on good straight lines with no indication of curvature in the temperature range 458–484 K. There is no apparent evidence for other than a thermally activated process (or processes), but this is not inconsistent with thermal population of the gauche conformer and thermal excitation of the relevant vibrational modes in the description of vibrationally assisted tunneling, as described by eq 1.

The temperature-dependent primary kinetic isotope effect, which was obtained from the least-squares lines in Figure 1, is plotted against temperature as the solid line in Figure 3. The temperature dependence of the ratio k_H/k_D is rather uncertain: it amounts to a change of only 9–10% in the observed ratio over a 26 K range while the error in the slope is about 50% according to the error estimates of Roth and König (6 ± 3 kJ·mol^{-1}).[1] Therefore, a discussion of the temperature dependence of the isotope effect seems inappropriate.

It is clear from Figure 3 that the deuterium isotope effect is large—about 5 in the temperature range investigated. Representative values[6] calculated by the method of periodic orbits are plotted for comparison as the alternating long and short dashes in Figure 3. They fall short of the observed values by a factor of about 2. Dewar, Healy, and Ruiz spent 30 h of Cray-XMP/24 cpu time to perform frequency calculations at the MP2/3-21G level in order to demonstrate that this discrepancy cannot be attributed merely to errors in the calculated frequencies. The resulting value of k_H/k_D at 473 K differed from the earlier result by 1%.

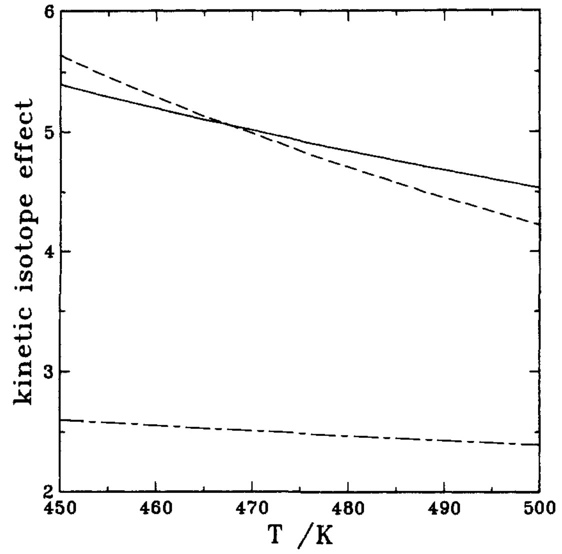


Figure 3. The temperature dependence of the ratio k_H/k_D for *cis*-1,3-pentadiene. The solid line was obtained from the least-squares lines in Figure 1. The large dashes represent the present calculation with vibrationally assisted tunneling. The alternating long and short dashes correspond to an earlier calculation based on the method of periodic orbits, the results of which were reported in ref 6. The results of calculations based on Bigeleisen's equation, which appear in ref 7, are similar to the latter.

Table III Kinetic Isotope Effect and Hydrogen-Transfer Rate Constants for *cis*-1,3-Pentadiene[a]

	k_H/k_D			$k_H/10^{-6}$ s^{-1}	
T/K	obs	VAT	no VAT	obs	VAT
100		6×10^3	2×10^4		0.00
425		6.7	1×10^4		0.34
450	5.4	5.6	1×10^4	0.64	1.4
475	4.9	4.8	8×10^3	5.3	5.3[b]
500	4.5	4.2	6×10^3	36	18

[a] The heading "obs" designates values obtained from least-squares fits to Arrhenius plots of the experimental data in ref 1. The heading "no VAT" designates values from calculations with only zero-point motion in the promoting mode. [b] The calculated values have been scaled to obtain agreement with the observed k_H at 475 K.

The ratios k_H/k_D calculated from eq 1 are listed in Table III and plotted as the dashed line in Figure 3. These values are completely consistent with the observed kinetic isotope effect. Corresponding values of k_H itself are also listed in Table III. The absolute rate constant depends upon a scaling parameter for which we have no accurate theoretical estimate in the present case. Thus, the temperature and isotope dependences of the calculated rate constant are well determined by the present method, but the absolute values have been scaled to fit the experimental value of k_H at 475 K.

The calculated temperature dependence of k_L is somewhat weaker than that found experimentally: the derived activation energy of 94 kJ·mol^{-1} is lower than the experimental value of 148 kJ·mol^{-1}. From the factorization in eq 1, about 11 kJ·mol^{-1} is associated with the conformational energy difference ΔE. The activation energy associated with the process **1b** → **2b** is then 83 kJ·mol^{-1}. In the usual formulation of the kinetic isotope effect,[9] the activation energy drops out of the equation for $\tilde{k}_L(T)$ to leave a ratio of partition functions and transmission coefficients; the kinetic isotope effect itself does not depend on the activation energy. In previous calculations,[6,7] the temperature dependence of $\tilde{k}_L(T)$ was given similarly by the product of a tunneling rate and a Boltzmann factor associated with twisting of the methylene terminus. For example, Dormans and Buck obtained an activation energy of 125 kJ·mol^{-1}, of which 94 kJ·mol^{-1} arises rather arbitrarily from the methylene twist.[7] (To this value, about 26 kJ·mol^{-1} should have been added presumably, which is the energy of their C_s s-cis conformation relative to the s-trans conformer.) Thus, the activation energy derived from such calculated rate constants is in better agreement with experiment than the present results, but only a relatively small fraction (31 in 125 kJ·mol^{-1}) is associated with $\tilde{k}_L(T)$. On the other hand, the temperature dependence in the present calculations arises principally from the migration process itself (83 in 94 kJ·mol^{-1}).

It is clear that the temperature dependence of the transfer rate constant belies the fact that tunneling is important in this reaction. In fact, because the more stable s-trans conformer is unreactive, the conformational equilibrium ensures that the temperature dependence of the rate constant will *never* exhibit the temperature-independent limiting behavior that is characteristic of ground-state tunneling at low temperatures. The migration process, which is monitored by observing the s-trans conformer, is nonetheless dominated by tunneling within the gauche conformer, which is unmistakably responsible for the kinetic isotope effect.

In order to demonstrate that this tunneling is vibrationally assisted, calculations were performed in which only the ground state of the promoting mode was populated while the CL-stretching modes were allowed thermal populations. Thus the thermal motion of the promoting mode was essentially frozen out. Some results appear in Table III. At 100 K, k_H is about an order of magnitude smaller when vibrational assistance is excluded. At 475 K, k_H is about *fifteen orders of magnitude* smaller in the absence of VAT. There is a concomitant increase in the kinetic isotope effect because the effect on the magnitude of the resulting, effectively one-dimensional barrier is enormous. Moreover, the zero-point motion of the skeletal mode is not sufficient to produce a significant increase in the rate constant, contrary to the suggestion of LeRoy.[15] Even if the present calculations are quantitatively incorrect, the observed isotope effect cannot be explained without the involvement of tunneling. Because the molecular geometry of the gauche conformer makes ground-state tunneling improbable, vibrationally assisted tunneling must occur.

Because the structural and dynamical information pertains to the reactant and product species and not to intermediates, it should be clear that the present calculations do not distinguish between the classical transition-state structures that have been proposed for this process. In previous work[4-9] these structures have received undue attention. In the case of hydrogen migrations, the minimum-energy path on the Born–Oppenheimer potential energy surface does not provide an adequate description of the dynamics. This fact has been emphasized many times.[16] If the saddle point on the minimum-energy path is designated as the transition state, much of its significance is lost when tunneling is important: the migration process can avoid such a transition state altogether. The failure of previous attempts to reproduce the observed isotope effect in the case of *cis*-1,3-pentadiene arose because the chosen methods did not account adequately for contributions along paths other than the minimum-energy path. Motions orthogonal to this path, which are passive in most reactions, may contribute strongly in the case of hydrogen migration. In polyatomics, vibrationally assisted hydrogen transfer is the rule rather than the exception.

Acknowledgment. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada and the Science and Engineering Research Board of McMaster University. Some the calculations reported herein were performed on the Cray-XMP/24 supercomputer at the Ontario Centre for Large-Scale Computation. We are grateful to the referees for some useful criticisms.

---

(15) LeRoy, R. J. *J. Phys. Chem.* **1980**, *84*, 3508.

(16) For example: Ovchinnikova, M. Ya. *Chem. Phys.* **1979**, *36*, 85. Babamov, V. K.; Marcus, R. A. *J. Chem. Phys.* **1981**, *74*, 1790. Kaye, J. A.; Kupperman, A. *Chem. Phys. Lett.* **1981**, *77*, 573. Manz, J.; Römelt, J. *Chem. Phys. Lett.* **1981**, *81*, 179. Garrett, B. C.; Truhlar, D. G.; Wagner, A. F.; Dunning, T. H., Jr. *J. Chem. Phys.* **1983**, *78*, 4400. Garrett, B. C.; Truhlar, D. G. *J. Chem. Phys.* **1983**, *79*, 4931. Garrett, B. C.; Abusalbi, N.; Kouri, D. J.; Truhlar, D. G. *J. Chem. Phys.* **1985**, *83*, 2252. Carrington, T., Jr.; Miller, W. H. *J. Chem. Phys.* **1986**, *84*, 4364. Miller, W. H.; Ruf, B. A.; Chang, Y.-T. *J. Chem. Phys.* **1988**, *89*, 6298.