Vibrationally Assisted Tunnelling (VAT) in a 1,5 Hydrogen Shift?

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Vibrationally assisted tunnelling (VAT), kinetic isotope effect, and MINDO/3 calculations are reported for the 1,5 hydrogen migration of penta-1,3-diene; from these calculations it is demonstrated that tunnelling affects the kinetic isotope effect of this rearrangement and that the 1,5 shift should proceed *via* VAT almost exclusively at 498 K.

The mechanism of the 1,5 sigmatropic shift of penta-1,3-diene (**1**) has been of considerable interest recently owing to the suggestion of Kwart[1] that the transition state (**3**) is linear. This suggestion has been shown by several authors to be incorrect[2] and Kwart's temperature-dependent kinetic isotope effect theory[1] has been questioned.[3] The purpose of this communication is to assess the importance of tunnelling in the case of the 1,5 sigmatropic shift of penta-1,3-diene.

Our MINDO/3[4] calculations for (**1**) → (**2**) led to a chair-type transition state (**4**) similar to those reported previously.[2] Kwart's structure (**3**), besides being higher in energy by 84 kcal/mol,† was not even a stationary point on the potential surface. Table 1 compares our calculated activation parameters and calculated deuterium kinetic isotope effect[5] with those observed. The calculated heat of activation ($\Delta H^{\ddagger}$) is 10 kcal/mol larger than that observed by Roth and König[6] while the calculated deuterium kinetic isotope effects are about half those observed[6] and also show a smaller dependence on temperature than the experimental values.

The error in $\Delta H^{\ddagger}$ values is unusually large for a reaction of this kind, though admittedly not outside the error limits for MINDO/3 calculations. The results for the kinetic isotope effect calculations are, however, surprising. While the MINDO/3 values for deuterium kinetic isotope effects are usually somewhat too small, owing to neglect of tunnelling, the differences have always been far less than those found here.[5] The observed and calculated[5] values for other reactions

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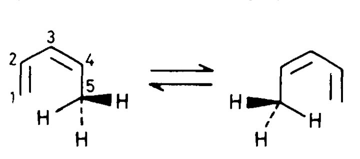
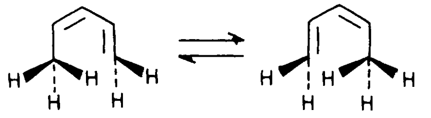
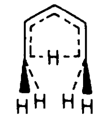
† 1 cal = 4.184 J.



(1) (2)

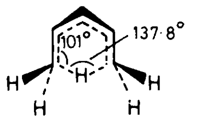


(1a) (2a)



C_{2v}

(3)



C_s

(4)

Table 1. MINDO/3 enthalpies, entropies of activation, and kinetic isotope effects for the conversion of (**1**) into (**2**).

	k_H/k_D for (**1**)	
T/K	calc.	obs.[a]
460	2.55	5.35
470	2.51	5.18
480	2.47	5.01
490	2.43	4.87
500	2.39	4.73

ΔH_f(act.)[b]		ΔS(act.)[c]	
calc.	obs.	calc.	obs.
45.2	35.4[a]	−10.3	−7.1[a]

[a] See ref. 6. [b] Units kcal/mol. [c] Units cal K^{-1} mol^{-1}.

involving intramolecular migration of hydrogen have moreover been similar to our calculated values for (**1**) → (**2**) and much less than those observed by Roth and König. Furthermore, as Roth and König pointed out, Arrhenius extrapolation of their kinetic isotope effect leads to a value at room temperature (298 K) of 12.2, which seems quite unreasonably large.

While these discrepancies could be explained immediately if the conversion of (**1**) into (**2**) took place largely by tunnelling in the temperature range studied (460—500 K), direct tunnelling from the ground state of (**1**) to the ground state of (**2**) seems out of the question because of the large change in geometry involved. Tunnelling might, however, be possible from vibrationally excited forms of (**1**), these being able to adopt geometries similar to those of analogously excited forms of (**2**), apart from the position of the migrating hydrogen atom. Tunnelling would then involve *only* the migrating hydrogen atom. Unlike ground state tunnelling, such a reaction would involve activation, corresponding to the necessary vibrational excitation. Such a process may be conveniently described as vibrationally assisted tunnelling (VAT).

Table 2. Calculated classical and tunnel rates *vs.* observed rate at 498 K.

T/K	ΔS(calc.)/ cal K^{-1} mol^{-1}	k(calc.)/ s^{-1}	k(obs.)[a]/ s^{-1}	k(tunnel)/s^{-1} (corrected[c])
498 (H)	−11.68	1.148×10^{-9}	3.25×10^{-5}	8.44×10^{-5}[b]
498 (D)	−11.97	8.257×10^{-10}	5.96×10^{-6}	5.80×10^{-7}[b]

[a] See ref. 6. [b] See refs. 8 and 9 (using periodic orbits). [c] Calculated vibrational frequencies corrected by 10% (see ref. 10). Vibrational frequencies used: C–H stretch 3457.5 cm^{-1}, imaginary frequency for H transfer 1691.6, C–D stretch 2549.7, and imaginary frequency for D transfer 1358.87.

While the possibility of such processes has been recognised for many years, few examples seem to have been cited and the methods used are usually rather complicated.[7] Treatment of VAT in terms of a one-dimensional barrier also seems dubious when extensive changes in geometry are involved, as is the case here. It occurred to us that a good approximation might be obtained, in the case of (**1**) by first constraining the other atoms to adopt a geometry (**1a**) favourable to tunnelling, the motion of the migrating hydrogen then being treated as a one-dimensional process. The overall rate is then written as a product of the tunnelling rate for the hydrogen migration and a Boltzmann factor ($e^{-E/RT}$) corresponding to the energy (E) needed to distort (**1**) to (**1a**). A reasonable choice for the geometry seemed to be one derived from that of the transition state (**4**) by fixing the positions of all atoms other than the migrating H(D) and optimising that of the latter, so that it attaches itself to C(1) (**1a**) or C(5) (**2a**). The tunnelling rate for (**1a**) to (**2a**) was calculated by the method of periodic orbits,[8] which seems to give reasonable estimates of tunnelling rates in degenerate rearrangements.[9] The energy (E) needed to distort (**1**) to (**1a**) or (**2**) to (**2a**) was 21.1 kcal/mol. The overall VAT rates at 498 K, corrected by the corresponding Boltzman factor, are shown in Table 2. As the comparison in Table 2 shows, the tunnelling rate for hydrogen is comparable with the rates of rearrangement observed by Roth and König[6] in the range 458—483 K.

The procedure used here to estimate VAT rates is of course very crude. It can be expected, and is intended, only to indicate their orders of magnitude. With this proviso, our calculations do seem strongly to support our suggestion that the rearrangement of (**1**) to (**2**) by migration of hydrogen takes place largely by VAT in the temperature range used by Roth and König. If so, their extrapolation of the kinetic isotope effect to room temperature was not valid because their k_H corresponds to a composite of two processes with different activation energies. Tunnelling should also become important for deuterium migration at lower temperatures. Our calculations indeed imply that the migration of H and D should both take place exclusively by VAT at 298 K. The ratio of VAT rates is the same at all temperatures according to our model, being 145 : 1, and both should show the same dependence on temperature.

The work reported here clearly has general implications concerning the interpretation of rates of hydrogen migrations. Since tunnelling in the conventional sense, between vibronic ground states, should take place at the same rate at all temperatures, it has usually been assumed that any contribution by tunnelling to the rate of a reaction is essentially independent of temperature. Our results indicate a third possible contributing mechanism in such cases, one which involved tunnelling but at the same time may show a large temperature dependence corresponding to the vibrational excitation involved. The procedure we have suggested for calculating VAT rates may also be useful as a guide to its possible significance in specific cases.

This work was supported by the Air Force Office of Scientific Research and the Robert A. Welch Foundation. The calculations were carried out using a DEC VAX 11-780 computer purchased with funds provided by the National Science Foundation and The University of Texas at Austin.

Received, 24th July 1984; Com. 1083

References

1 H. Kwart, M. W. Brechbiel, R. M. Acheson, and D. C. Ward, *J. Am. Chem. Soc.,* 1982, **104**, 4671; H. Kwart, *Acc. Chem. Res.*, 1982, **15**, 401.
2 B. A. Hess and L. J. Schaad, *J. Am. Chem. Soc.,* 1983, **105**, 7185; R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.,* 1972, **95**, 9107; N. G. Rondan and K. N. Houk, *Tetrahedron Lett.*, 1984, 2519.
3 A. A. Vitale and J. San Filippo, Jr., *J. Am. Chem. Soc.*, 1982, **104**, 7341.
4 R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285, 1294.
5 M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, 1977, **99**, 8343; S. B. Brown, M. J. S. Dewar, G. P. Ford, D. J. Nelson, and H. S. Rzepa, *J. Am. Chem. Soc.*, 1978, **100**, 7832; E. Canadell, J. P. Poblet, and S. Olivella, *J. Phys. Chem.*, 1983, **87**, 424.
6 von W. R. Roth and J. König, *Liebigs Ann. Chem.*, 1966, **699**, 24; von W. R. Roth, *Chimia,* 1966, **229**, 20.
7 See *e.g.*, T. E. Sharp and H. S. Johnston, *J. Chem. Phys.*, 1962, **37**, 1541; H. S. Johnston and D. Rapp, *J. Am. Chem. Soc.*, 1961, **83**, 1; H.-H. Limbach, J. Hennig, and J. Stulz, *J. Chem. Phys.*, 1983, **78**, 5432 and references cited therein; S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer, III, *J. Am. Chem. Soc.*, 1981, **103**, 1900.
8 (a) M. S. Child, *Mol. Phys.*, 1967, **12**, 401; (b) W. H. Miller, *J. Phys. Chem.*, 1979, **83**, 960; (c) J. Bicerano, H. F. Schaefer, III, and W. H. Miller, *J. Am. Chem. Soc.*, 1983, **105**, 2550.
9 M. J. S. Dewar, K. M. Merz, Jr., and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1984, **106**, 4040, see also ref. 8(c).
10 M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, 1977, **99**, 1685.