Mechanisms of Elimination Reactions. 30. The Contributions of Tunneling and Heavy-Atom Motion in the Reaction Coordinate to Deuterium Kinetic Isotope Effects in Eliminations from 2-Phenylethyl Derivatives[1,2]

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Abstract: The temperature dependence of the rates of elimination of 2-phenylethyltrimethylammonium (**1**) and 2-phenylethyl-*2,2-d*$_2$-trimethylammonium (**1**-*2,2-d*$_2$) bromides with hydroxide ion in mixtures of water and dimethyl sulfoxide and with ethoxide ion in ethanol reveals abnormalities in the Arrhenius parameters that are characteristic of tunneling. Fitting a temperature dependence calculated from the Bell theory of tunneling to the observed temperature dependence permits the evaluation of the tunnel correction to the isotope effect, Q_{tH}/Q_{tD}, and the semiclassical isotope effect, the effect in the absence of tunneling, $(k_H/k_D)_s$. The tunnel corrections are modest but by no means negligible, and the semiclassical isotope effects are well below the values predicted for a transition state with a symmetrically located proton, even though k_H/k_D and $(k_H/k_D)_s$ show maximum values in 40% dimethyl sulfoxide. It is suggested that the contribution of heavy-atom motion to the motion along the reaction coordinate keeps the semiclassical isotope effect small. Examination of selected data from the literature reveals a similar pattern of moderate tunnel corrections and below-maximum semiclassical isotope effects. The implications of these results for the interpretation of deuterium kinetic isotope effects in slow proton transfers are discussed.

There is no reason to doubt that tunneling occurs to some extent in chemical reactions, but there has been a great deal of controversy over the experimental evidence in specific instances. Since tunneling is predicted to be more important the lighter the system involved, it should make deuterium or tritium kinetic isotope effects larger than they would otherwise be. Very few secure examples are to be found in the literature, however, of kinetic hydrogen isotope effects so large that one is *compelled* to invoke tunneling to account for them. As a result, this criterion leads to the conclusion that tunneling is a rare and exceptional phenomenon.

Another criterion for tunneling that lacks the bias of the first one is the temperature dependence of the isotope effect. In the presence of tunneling the difference in Arrhenius activation energies $E_{aD} - E_{aH}$ is expected to exceed ca. 1.2 kcal mol^{-1}, and the ratio of Arrhenius preexponential factors, A_{aH}/A_{aD}, is expected to be substantially below unity.[3] While values of A_{aH}/A_{aD} as low as 0.5 can in principle be explained without tunneling, model calculations show that the realistic lower limit lies in the range 0.7–0.9.[4,5]

Although this criterion can provide a clear qualitative indication of tunneling, its application has been restricted by a paucity of really precise values for the Arrhenius parameters. Many studies of the temperature dependence of deuterium kinetic isotope effects involve a temperature range of only 10–20 °C, and no more than two or three temperatures within that range. Unless the rate constants are uncommonly precise, the resulting A_{aH}/A_{aD} values are so uncertain as to be of little use. A marked exception to this picture is the elegant study by Shiner and Smith of the bimolecular elimination reaction of 2-phenylpropyl-*2-d* bromide with ethoxide ion in ethanol over a 50 °C range.[6] The results provided clear evidence for tunneling in this typical E2 reaction.

We have for some time been interested in acquiring evidence on the suggestion of Bell, Sachs, and Tranter[7] that tunneling might be responsible for the maxima sometimes observed in k_H/k_D values for proton transfer reactions when the basicity of the attacking base or the acidity of the substrate is varied. Evidence from carbon isotope effects[8] suggested a contribution of tunneling in the E2 reaction of 2-phenylethyltrimethylammonium ion (**1**) with hydroxide ion in mixtures of dimethyl sulfoxide (Me_2SO) and water (eq 1).

$$\mathrm{PhCH_2CH_2NMe_3^+ + OH^- \xrightarrow{Me_2SO\text{-}H_2O} PhCH{=}CH_2 + NMe_3 + H_2O} \quad (1)$$

Consequently, we decided to carry out careful studies of the temperature dependence of the rates of reaction of **1** and **1**-*2,2-d*$_2$. A maximum in k_H/k_D as the Me_2SO concentration is varied has been observed near 40% Me_2SO for this reaction.[9]

The reaction of each substrate was studied in 30, 40, and 50% Me_2SO over a range of at least 25 °C at intervals of 5 °C. A still wider range would have been desirable, but we restricted ourselves to reactions that were neither too fast nor too slow to follow with a reproducibility of 1–3% for the rate constants. Results in 40% Me_2SO are given in Table I. All of the data were fitted to the Arrhenius equation by a linear regression program. The resulting parameters, as well as those for reaction with ethoxide ion in ethanol, are given in Table II.

The Arrhenius parameters for the isotope effects, given in the first two lines of Table III, provide clear evidence for tunneling in all cases except, perhaps, the reaction with ethoxide ion in ethanol. The k_H/k_D values in line 3, however, are of entirely normal magnitude. Even the maximum value at 40% Me_2SO is somewhat below that predicted at 50 °C for loss in the transition state of the zero-point energy difference associated with a carbon–protium vs. a carbon–deuterium stretching vibration of the substrate (ca. 6.5). The actual contribution to the isotope effect from zero-point energy must be lower still if tunneling is significant.

To assess the magnitude of the tunnel effects, we employed a computer program by Caldin and Mateo.[10] The program assumes that the Arrhenius equation correctly represents the temperature dependence of a reaction with tunneling if a tunnel correction factor, Q_t, is included (eq 2).

$$k_H = Q_{tH} A_H \exp(-E_H/RT) \quad (2)$$

It is further assumed that $A_H = A_D$ in the absence of tunneling, so that the temperature dependence of the isotope effect can be represented by

$$k_H/k_D = (Q_{tH}/Q_{tD}) \exp[(E_D - E_H)/RT] \quad (3)$$

The tunnel corrections are calculated by using the first four

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Table I. Temperature Dependence of the Rate Constants for the Reaction of 2-Phenylethyltrimethylammonium and 2-Phenylethyl-*2,2-d*$_2$-trimethylammonium Bromides (0.004 M) with Hydroxide Ion (0.04 M) in 40% Dimethyl Sulfoxide

T, °C	$k_H \times 10^4$, $M^{-1}\,s^{-1}$	$k_D \times 10^4$, $M^{-1}\,s^{-1}$
30	4.15	
	4.18	
40	16.1	2.63
	16.5	2.73
45	30.0	5.30
	30.8	5.40
50	53.8	9.68
	53.3	9.80
55	94.5	18.6
	95.8	18.8
60	177	34.5
	179	35.3
70		114
		114

terms of the Bell equation

$$Q_t = (\tfrac{1}{2}u_t/\sin \tfrac{1}{2}u_t) - u_t \exp(E/RT) \times \left(\frac{y}{2\pi - u_t} - \frac{y^2}{4\pi - u_t} + \frac{y^3}{6\pi - u_t} - \ldots\right) \quad (4)$$

where

$$u_t = h\nu_t/kT = (h/kT)[E^{1/2}/\pi a(2m)^{1/2}] \quad (5)$$

and

$$y = \exp(-2\pi E/h\nu_t) \quad (6)$$

It is assumed that $m_H = 1$ amu and $m_D = 2$ amu, and the values of the barrier heights (E_D and E_H) and the barrier half-widths (a_D and a_H) are systematically varied, subject to the constraint that the barrier curvatures, $E^{1/2}/a$, be the same for the protium and deuterium species. (The curvature of the inverted parabola at its vertex is mathematically defined as $-2E/a^2$, but we prefer to use $E^{1/2}/a$ for convenience.) In this way, values of the barrier heights and half-widths that give the best fit of the calculated to the observed temperature dependence can be determined, and from them and eq 3-6 values of the tunnel corrections Q_{tH} and Q_{tD} calculated at any desired temperatures within the temperature range.

The Caldin-Mateo program gives fits to our results that are well within experimental error, although fits of comparable precision are found with numerous sets of barrier heights and half-widths as long as the curvatures, $E^{1/2}/a$, and the differences in barrier heights, $E_D - E_H$, remain about the same. The reason becomes evident on careful reflection. One is attempting to fix *four* parameters, or *three* with the constraint that $E^{1/2}/a$ be the same for both isotopic species, with the aid of only *two* quantities derived from experiment, $E_{aD} - E_{aH}$ and A_{aH}/A_{aD}. Obviously one cannot hope to fix a unique set of barrier heights and barrier widths, but one can still fix the two combinations of parameters $E^{1/2}/a$ and $E_D - E_H$. These in turn suffice to fix unique values of Q_{tH} and Q_{tD}, provided that the first term of eq 4 adequately represents the data. Such is the case with our experimental results, which give u_t values substantially less than 2π in all cases. When the tunnel correction is large enough to require two or more terms of eq 4, absolute values of E_D and E_H are needed.

If separate values of the Bell equation parameters are desired, they can be obtained as follows. Once the fit utilizing eq 3 has been carried out, the resulting Q_{tH} values can be substituted into a slightly rearranged version of eq 2

$$k_H/Q_{tH} = A_H \exp(-E_H/RT)$$

A conventional Arrhenius plot of ln (k_H/Q_{tH}) vs. $1/T$ then gives E_H and the "true" (without tunneling) A_H, and E_D and A_D can be analogously evaluated. Since $E^{1/2}/a$ is already known, a_H and a_D can be calculated. This additional infor-

Table II. Activation Parameters for the Reaction of 2-Phenylethyltrimethylammonium and 2-Phenylethyl-*2,2-d*$_2$-trimethylammonium Bromides (0.004 M) with Base (0.04 M)[a]

	solvent/base			
	30% Me$_2$SO/OH$^-$	40% Me$_2$SO/OH$^-$	50% Me$_2$SO/OH$^-$	EtOH/EtO$^-$
$A_H \times 10^{-14}$	0.489 ± 0.163	3.54 ± 0.93	0.00675 ± 0.00138	337 ± 49
$A_D \times 10^{-14}$	1.80 ± 0.498	10.5 ± 2.2	0.0317 ± 0.0078	474 ± 120
E_{aH}, kcal mol^{-1}	24.88 ± 0.22	24.86 ± 0.17	19.71 ± 0.13	27.84 ± 0.09
E_{aD}, kcal mol^{-1}	26.69 ± 0.19	26.64 ± 0.14	21.58 ± 0.15	28.76 ± 0.17
$\Delta S^{\ddagger}_H$, cal mol^{-1} K^{-1}	1.87 ± 0.66	5.91 ± 0.52	−6.53 ± 0.41	14.9 ± 0.3
$\Delta S^{\ddagger}_D$, cal mol^{-1} K^{-1}	4.43 ± 0.55	8.01 ± 0.42	−3.46 ± 0.48	15.6 ± 0.5
temp range, °C, for H	50-75	30-60	30-60	35-60
temp range, °C, for D	55-80	40-70	30-60	45-70

[a] From linear-regression fits to the Arrhenius equation of experimental rate constants determined at 6-7 temperatures, 1-3 points per temperature. Replicate rate constants almost always agreed within 1-3%. Deviations are standard deviations.

Table III. Tunnel Corrections for the Reaction of 2-Phenylethyltrimethylammonium and 2-Phenylethyl-*2,2-d*$_2$-trimethylammonium Bromides with Base[a]

	solvent/base			
	30% Me$_2$SO/OH$^-$	40% Me$_2$SO/OH$^-$	50% Me$_2$SO/OH$^-$	EtOH/EtO$^-$
$E_{aD} - E_{aH}$, kcal mol^{-1}	1.81 ± 0.29	1.78 ± 0.22	1.87 ± 0.20	0.92 ± 0.19
A_H/A_D	0.27 ± 0.12	0.34 ± 0.11	0.21 ± 0.07	0.71 ± 0.21
k_H/k_D,[b] 50 °C	4.65	5.42	3.93	2.96
Q_{tH}/Q_{tD}, 50 °C	2.07	1.76	1.94	1.29
Q_{tH}, 50 °C	3.53	2.75	3.20	1.63
$(k_H/k_D)_s$,[c] 50 °C	2.24	3.08	2.03	2.29
$E_D - E_H$, kcal mol^{-1}	0.519	0.722	0.454	0.530
$E^{1/2}/a$, kcal$^{1/2}$ mol$^{-1/2}$ Å^{-1}	7.01	6.47	6.81	4.76

[a] From fits to data of Table II using eq 10 and 11. Assumes $m_H = 1$, $m_D = 2$. [b] Calculated values from the fitting process. They agree with values computed from the Arrhenius parameters to well within 2%. [c] Semiclassical isotope effect, $(k_H/k_D)/(Q_{tH}/Q_{tD})$.

mation can clearly not be obtained in cases where k_H/k_D values from competitive methods are the input, and the separate k_H and k_D values are not known. It should also be noted that a unique set of E_H, E_D, a_H, and a_D values can be obtained only with respect to specific assumed values of the effective masses m_H and m_D.

It is possible to devise a much simpler program for the determination of tunnel corrections than that of Caldin and Mateo when the first term of eq 4 is adequate. Bell[11] has shown that the definition of E_a, eq 7,

$$E_a = RT^2 \, \mathrm{d} \ln k/\mathrm{d}T \qquad (7)$$

may be used to express the tunnel correction in terms of the differences between the apparent activation energy E_a and the "true" barrier height E, and between the apparent, $\ln A_a$, and true, $\ln A$, Arrhenius intercepts:

$$E_a - E = RT(\tfrac{1}{2}u_t \cot (\tfrac{1}{2}u_t) - 1) \qquad (8)$$

$$\ln A_a - \ln A = \ln (\tfrac{1}{2}u_t/\sin \tfrac{1}{2}u_t) + \tfrac{1}{2}u_t \cot (\tfrac{1}{2}u_t) - 1 \qquad (9)$$

If one assumes that $A_H = A_D$ in the absence of tunneling, one gets

$$\ln (A_{aH}/A_{aD}) = \ln (u_{tH} \sin \tfrac{1}{2}u_{tD}/u_{tD} \sin \tfrac{1}{2}u_{tH}) + \tfrac{1}{2}u_{tH} \cot \tfrac{1}{2}u_{tH} - \tfrac{1}{2}u_{tD} \cot \tfrac{1}{2}u_{tD} \qquad (10)$$

and

$$E_D - E_H = (E_{aD} - E_{aH}) - RT(\tfrac{1}{2}u_{tD} \cot \tfrac{1}{2}u_{tD} - \tfrac{1}{2}u_{tH} \cot \tfrac{1}{2}u_{tH}) \qquad (11)$$

While eq 10 cannot be solved explicitly for u_{tH} and u_{tD}, it is possible to arrive at values by trial and error by making some assumption concerning the relation between u_{tH} and u_{tD}. It is convenient to assume $u_{tD} = u_{tH}/\sqrt{2}$, which is equivalent to assuming $m_H = 1$ amu and $m_D = 2$ amu. Then u_{tH} is varied until eq 10 reproduces A_{aH}/A_{aD} from experiment, and $E_D - E_H$ is evaluated from eq 11. The barrier curvature, $E^{1/2}/a$, is then obtained from eq 5. The temperature used in eq 5 and 11 is taken as that at the midpoint of the experimental range. Q_{tH} and Q_{tD} values can then be calculated.

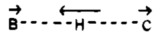
Before proceeding to the results of such fits, we should consider possible limitations on their reliability. The Bell theory of tunneling is open to criticism because it uses a one-dimensional parabolic barrier. The assumption of a one-dimensional barrier is necessary if any progress is to be made in fitting theory to experiment in complex systems such as ours, but more realistic barrier shapes, such as Eckart or Gaussian barriers, can be used without insurmountable computational difficulty. It has been shown, however, that the first term of eq 4 gives essentially the same values of Q_t as are derived from the Eckart barrier when $u_t < 2\pi$ and the barrier height is substantial,[12] conditions that are fulfilled in our fits. The Eckart barrier gives the best fit to experimental data covering a much wider temperature range than ours.[13,14] Thus, a simple fit to eq 10 and 11 seems, within its aforementioned limitations, to be as good as any treatment that is currently feasible.

Table III lists the quantities derived from such fits to our data. The fits to eq 10–11 and to the Caldin–Mateo program give essentially the same results. We can now break down the overall isotope effect into the tunnel correction, Q_{tH}/Q_{tD}, and the semiclassical isotope effect, $(k_H/k_D)_s$, using eq 12.

$$k_H/k_D = (Q_{tH}/Q_{tD})(k_H/k_D)_s \qquad (12)$$

The semiclassical isotope effect is that part of the isotope effect due to zero-point energy effects. It is the quantity that we should consider in discussing the effect of the extent of hydrogen transfer in the transition state in terms of the Melander–Westheimer three-center model.[15,16] The maximum in the overall k_H/k_D clearly remains in $(k_H/k_D)_s$, which supports the Melander–Westheimer interpretation of variable isotope effects and argues against that of Bell et al.[7] who suggested that such maxima might arise from variations in the tunnel correction.

Qualitatively, one would expect the tunnel correction to depend on transition-state symmetry in about the same way as the zero-point energy contribution. When the proton is symmetrically located in the transition state, the motion along the reaction coordinate will be largely proton motion (**2**), while



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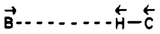
heavy-atom motion will contribute increasingly as the transition state becomes less symmetrical (see, for example, **3**, for



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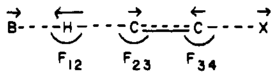
a very reactant-like transition state). The tunneling frequency, ν_t, of the Bell theory can be identified with the absolute value of the reaction coordinate frequency, $|\nu^{\ddagger}{}_L|$, at least within the approximations of the theory. Both the absolute magnitude of the reaction coordinate frequency, $\nu^{\ddagger}{}_{LH}$, and its isotopic sensitivity, $\nu^{\ddagger}{}_{LH}/\nu^{\ddagger}{}_{LD}$, should be greatest for the symmetrical transition state. There is no significant trend, however, in our Q_{tH}/Q_{tD} values in the Me_2SO–water mixtures. Either our separation of Q_{tH}/Q_{tD} and $(k_H/k_D)_s$ is not sufficiently precise to reveal the trend, or the change in Q_{tH}/Q_{tD} is more gradual than that in $(k_H/k_D)_s$. We hope to obtain further evidence on this point.

The most striking aspect of $(k_H/k_D)_s$ is that it remains so small, less than half the value of 6.5 (see above) estimated for a symmetrical transition state by the Melander–Westheimer treatment. Yet the isotope effect in 40% Me_2SO must be very close to the maximum value, so that the small zero-point energy contribution cannot be ascribed to an unsymmetrically located proton in the transition state. We believe that coupling of heavy-atom motion (C–C contraction and C–N stretching) with hydrogen motion in the reaction coordinate is the best explanation of our results. Model calculations showed some time ago[17,18] that such coupling should depress k_H/k_D values, but the present work is, to our knowledge, the first experimental evidence for this phenomenon.

The basis of the predictions from the calculations is as follows. To obtain a transition-state model in which one vibrational mode, the motion along the reaction coordinate, has the atoms moving in the proper phases to lead from reactants to products and has an imaginary frequency, the introduction of appropriate interaction force constants is necessary (**4**). This



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requirement is fulfilled by the three interaction force constants F_{12}, F_{23}, and F_{34}, provided they all have positive values. When $F_{12} \gg F_{23}$ and F_{34}, the motion along the reaction coordinate is largely proton motion and $(k_H/k_D)_s$ values of normal magnitude result. When F_{23} and F_{34} are increased at the expense of F_{12}, however, heavy-atom motion contributes increasingly to the motion along the reaction coordinate and $(k_H/k_D)_s$ becomes substantially less than the maximum value, even for a symmetrically located proton.

Comparison of the results in Me_2SO–water with those in ethanol shows that the overall k_H/k_D in the latter solvent is as small as it is mainly because of a smaller tunnel correction. The $(k_H/k_D)_s$ value is comparable to those in 30 and 50% Me_2SO. Previous discussions of k_H/k_D for the reaction of **1** with ethoxide in ethanol have considered the proton transfer

Table IV. Tunnel Corrections for Miscellaneous Elimination Reactions[a]

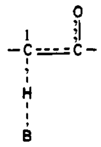
reaction, °C	k_H/k_D[b]	Q_{tH}/Q_{tD}	$(k_H/k_D)_s$[c]	Q_{tH}
$PhCHMeCH_2Br + EtO^-/EtOH$, 45 °C[d]	6.25	1.58	3.95	2.31
$PhCH_2CH_2Br + EtO^-/EtOH$, 50 °C[e]	6.13	1.47	4.18	2.03
$PhCH_2CH_2SMe_2^+ + OH^-/H_2O$, 60 °C[e]	4.67	1.63	2.87	2.42
p-$MeOPhCH_2CH_2Br + OH^-$/50.2% Me_2SO, 40 °C[f]	5.82	1.98	2.94	3.29
p-$MeOPhCH_2CH_2Br$ + *t*-BuOK/*t*-BuOH, 50 °C[g]	5.70	1.94	2.94	3.19
m-$NO_2PhCH_2CH_2Br$ + *t*-BuOK/*t*-BuOH, 50 °C[g]	7.34	1.38	5.34	1.82
$Ph_2CHCHCl_2 + MeO^-/MeOH$, 45 °C[h]	6.03	1.84	3.27	2.96

[a-c] See corresponding footnotes to Table III. [d] Reference 6. [e] Reference 20. [f] Reference 21. [g] Reference 22. [h] Reference 23.

to be well past the half-way point in the transition state.[19] The present results suggest that the degree of unsymmetry of the transition state may have been exaggerated.

To test the generality of our observations we searched the literature for studies of the temperature dependence of the isotope effect in E2 reactions of 2-arylethyl derivatives. We have mentioned above the results of Shiner and Smith[6] on the reaction of 2-phenylpropyl bromide with ethoxide in ethanol. This is almost the only case with a temperature range that is wide enough and that contains enough experimental points to give really precise Arrhenius parameters. We did find a few other cases that appeared to be reasonably reliable, even though most of them covered only a 20 °C range. The tunnel corrections and semiclassical isotope effects derived from fitting eq 10 and 11 to the observed temperature dependences are listed in Table IV.[6,20-22] Besides the data for 2-arylethyl derivatives, McLennan's study of the reaction of 2,2-diphenyl-1,1-dichloroethane with methoxide in methanol is included for comparison.[23]

The results in Tables III and IV strongly suggest that moderate tunneling accompanied by below-maximum semiclassical isotope effects is the rule rather than the exception in E2 reactions. This pattern may well be of still wider occurrence, for many slow proton transfers in organic chemistry involve heavy-atom reorganization not unlike that in the E2 reaction as part of the motion along the reaction coordinate. The formation of enolate ions from carbonyl compounds (**5**) and the ionization of nitroalkanes (**6**) are particularly good examples.



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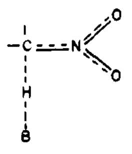

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Table V. Tunnel Correction as a Function of Effective Mass for the Reaction of 2-Phenylethyltrimethylammonium and 2-Phenylethyl-*2,2-d*$_2$-trimethylammonium Bromide with Hydroxide Ion in 40% Dimethyl Sulfoxide[a]

m_H (eff)[b]	Q_{tH}/Q_{tD}	$(k_H/k_D)_s$[c]	Q_{tH}
1.0	1.76	3.08	2.75
1.1	1.74	3.12	2.80
1.2	1.72	3.14	2.86
1.3	1.70	3.22	2.89
1.4	1.68	3.23	2.95
1.5	1.66	3.28	2.98

[a] From fits to data of Table II using eq 10 and 11. [b] Assumes m_D(eff) = m_H(eff) + 1. [c] See corresponding footnote to Table III.

There is not a wide range to the tunnel corrections in Tables III and IV, and the reactions and reaction conditions are too assorted for one to draw any clear conclusions about possible trends. One interesting comparison is afforded by the fifth and sixth entries in Table IV. There is a distinct difference in tunnel corrections between these two reactions, which means that a Hammett ρ value derived from the rate constants for these reactions and the appropriate σ values would contain a contribution from tunneling as well as from the usual polar substituent effects. Since tunneling is a purely kinetic phenomenon which cannot affect the ionization equilibria used to establish σ values, it should be factored out of rates before they are treated by a rate–equilibrium correlation such as the Hammett equation. A two-point "tunneling ρ" can be estimated from these data as:

$$\rho = \frac{\log (Q_{tH}^{p\text{-OMe}}/Q_{tH}^{m\text{-NO}_2})}{\sigma_{p\text{-OMe}} - \sigma_{m\text{-NO}_2}} = -0.25$$

Thus the ρ value without tunneling would be 0.25 more than the apparent overall ρ value. This difference is unlikely to affect the qualitative interpretation of ρ, but there are situations where a difference of this magnitude could change qualitative interpretations. An example would be orientation in E2 reactions, where a substantial shift in proportions of isomeric products could result.

One aspect of our results that deserves further comment is the role of the effective mass along the reaction coordinate. We pointed out earlier[2] the troublesome paradox that the fits assume m_H = 1 amu and m_D = 2 amu; yet the results suggest that the effective masses should be greater than the masses of protium and deuterium because of heavy-atom involvement in the reaction coordinate motions. We have since found that the failure of larger m_H and m_D values to give good fits to eq 3 was simply a consequence of the order in which the parameters were varied: once $E_D - E_H$ is fixed, those m_H and m_D values used in finding it become optimum values which cannot be varied without worsening the fit.

Table V shows the results of a treatment using eq 10 and 11 which started with m_H values from 1.0 to 1.5 amu, assumed $m_D = m_H + 1$, and then determined the values of $E_D - E_H$ and $E^{1/2}/a$ that gave the best fits with the assumed masses. While the precision of the fits varied somewhat, there was no clear superiority with any given value of m_H. This should not be surprising. We noted above that the experimental quantities available, the slope and intercept of the Arrhenius plot, permit one to define a unique set of the parameters E_H, E_D, a_H, and a_D only when the temperature dependences of k_H and k_D are known individually. No further parameters can be fixed, and these four can be fixed only when specific values of m_H and m_D are assumed. Fortunately, this inability to determine the "true" values of the effective masses does not seriously affect the calculation of the tunnel correction. A variation in m_H from 1.0 to 1.5 amu produces less than a 10% change in Q_{tH} and Q_{tH}/Q_{tD}.

We know of only one report in the literature on the temperature dependence of hydrogen isotope effects in elimination reactions that contrasts markedly with the results in Tables III and IV. Koch, Dahlberg, McEntee, and Klecha studied base-promoted eliminations from the substrates **7**, where L =

$ArCLXCF_2X$

7

H, D, or T, Ar = C_6H_5 or p-ClC_6H_4, and X = Br or Cl.[24] The A_H/A_D values were reported to run from 1.5 to 4.8, and A_H/A_T values even higher. The temperature ranges and the number of points within these ranges were sufficient to give Arrhenius parameters with good precision, so most of the A_H/A_D and A_H/A_T values are clearly too large to be explicable by any reasonable simple model.[4] It thus appears likely that these reactions are not simple E2 processes. They could be two-stage E1cB reactions with internal return,[24] or mixed E2-E1cB reactions. Apparently abnormal A_H/A_D and A_H/A_T values can result if overall rate constants for complex reactions are treated as if they represented single elementary steps. Such abnormalities require, however, fortuitous combinations of relative rates and activation energies for the individual steps. It seems highly unlikely that they could account for the results in Tables III and IV, given the range of leaving groups, bases, and solvents represented.

Our results show that the practice of interpreting the magnitudes of primary hydrogen isotope effects in terms of the extent of hydrogen transfer in a linear three-center transition state is an oversimplification. A fairly large k_H/k_D (around 6 or more near room temperature) can probably still be safely taken as indicating a linear transition state with the hydrogen near the midpoint between the donor and acceptor atoms. Smaller values of k_H/k_D must, however, be ascribed a less definite meaning than in the past.

The fundamental factor behind low primary hydrogen isotope effects can best be appreciated by examination of the Teller-Redlich product rule expression for the transition state (eq 13).

$$\left(\frac{M^{\ddagger}_{H}}{M^{\ddagger}_{D}}\right)^{3/2}\left(\frac{A^{\ddagger}_{H}B^{\ddagger}_{H}C^{\ddagger}_{H}}{A^{\ddagger}_{D}B^{\ddagger}_{D}C^{\ddagger}_{D}}\right)^{1/2} = \frac{\nu^{\ddagger}_{LH}}{\nu^{\ddagger}_{LD}}\prod_{j}^{N^{\ddagger}}\left(\frac{m_{jH}}{m_{jD}}\right)^{3/2}\prod_{i}^{3N^{\ddagger}-7}\frac{\nu^{\ddagger}_{iH}}{\nu^{\ddagger}_{iD}} \quad (13)$$

The ratio of molecular masses (first term on the left) will be constant for any given reaction, and the ratios of the principal moments of inertia (second term on the left) will be essentially unaffected by minor changes in the geometry of the transition state, especially alterations in the position of the hydrogen being transferred. The left-hand side of eq 13 will thus remain essentially constant, and the product of ratios of atomic masses (second term on the right) will also be constant. A decrease in the ratio of frequencies for motion along the reaction coordinate, $\nu^{\ddagger}_{LH}/\nu^{\ddagger}_{LD}$, therefore must be accompanied by an increase in isotopic sensitivity of one or more of the real frequencies of the transition state (last term on the right). Consequently, a decrease in $\nu^{\ddagger}_{LH}/\nu^{\ddagger}_{LD}$ will increase the zero point energy difference between the isotopic transition states, and decrease the isotope effect.

An increase in the effective mass along the reaction coordinate decreases $\nu^{\ddagger}_{LH}/\nu^{\ddagger}_{LD}$. The contribution of heavy-atom motion to a complex reaction coordinate such as that for the E2 reaction is one way the effective mass can be increased. In addition, comparison of **3** and **2** reveals that heavy-atom motion is greater in an unsymmetrical than in a symmetrical linear three-center transition state. It can also be shown that heavy-atom motion is greater in a nonlinear than in a comparable linear three-center transition state. Thus, a small primary hydrogen isotope effect tells us that heavy-atom motion contributes to the motion along the reaction coordinate, but it does not tell us the precise mechanism of that contribution. The existence of isotope-effect maxima suggests, however, that the Melander-Westheimer linear three-center model[15,16] is often an adequate approximation to reality.

Neither our own data in Table III nor the literature data in Table IV show any general correlation between isotope effects and tunnel effects, although one might expect a large k_H/k_D to be associated with a large $\nu^{\ddagger}_{LH}/\nu^{\ddagger}_{LD}$. The tunnel correction depends on the absolute magnitude of $\nu^{\ddagger}_{L}$ as well as its isotopic sensitivity, however, and it is by no means obvious that these quantities need always vary in a parallel fashion for changes in the substrate, reagent, or solvent. Furthermore, the range of tunnel corrections in Tables III and IV is not wide, and experimental uncertainties in the Arrhenius parameters may be in part responsible for the lack of regularity.

Experimental Section

Solvents. Distilled water was refluxed with potassium permanganate and redistilled immediately prior to use. Fisher ACS dimethyl sulfoxide was refluxed over calcium hydroxide, and distilled in vacuo, the first 10% being discarded. It had mp 18-18.5 °C (lit.[25] 18.5 °C) and was stored in a tightly sealed amber bottle in a drybox. Mixtures of dimethyl sulfoxide and water were prepared gravimetrically. Percentages refer to mole percent. Absolute ethanol was refluxed over magnesium with a trace of iodine for 6 h and distilled, the first 10% being discarded. Water content was determined according to Vogel,[26] and batches containing more than 0.05% water discarded. The ethanol was stored in tightly sealed amber bottles for no longer than 1 week.

2-Phenylethyltrimethylammonium and 2-Phenylethyl-*2,2-d*$_2$-trimethylammonium Bromides. The preparations followed published procedures.[20] Both products had mp 238-239 °C (lit.[20] 238-239 °C).

Kinetics. A constant-temperature bath that kept the temperature constant within ±0.05 °C of the desired setting was used, and the temperatures checked against an NBS-calibrated thermometer. The substrate solution was equilibrated for at least 1 h in a 100-mL volumetric flask fitted with a septum cap. Enough 2 N sodium hydroxide solution was injected by syringe to make the final concentration 0.04 M. Aliquots of 0.1 mL were withdrawn by syringe and diluted with 5.0 mL of 99% ethanol, and the absorbance of the resulting solution was measured at 250 nm on a Beckman DB-GT UV spectrophotometer. The pseudo first-order rate constant was evaluated from the slope of a plot (6-8 points) of ln ($A_\infty - A_t$) vs. t, with A_∞ being taken after 6-10 half-lives. Temperatures were chosen so as to keep half-lives in the range of 15 min to 2 h. Reproducibility of rate constants was usually within 1-2%, and seldom worse than 3%. Runs were usually done in duplicate, but in a few cases were done only once or in triplicate.

Acknowledgments. We thank Professor Louis E. Friedrich, Mr. David Miller, and Mr. Richard Garcia-Kennedy for helpful discussions of the procedures for obtaining tunnel corrections from the Bell theory. We also thank Professor E. F. Caldin for a copy of the computer program described in ref 10.

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Regiocontrolled Hydrogenolysis of Strained σ Bonds. Application to the Synthesis of *syn*- and *anti*-Tricyclo[4.2.1.1^{2,5}]decane and Two Elusive Cyclopentadiene Dimers

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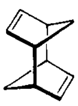
Abstract: Catalytic hydrogenation of hypostrophene over palladium on charcoal resulted in regiospecific σ bond hydrogenolysis to give *syn*-tricyclo[4.2.1.1^{2,5}]decane (**4**). Similar treatment of the *exo*-8-hydroxy derivative furnished *syn*-tricyclo[4.2.1.1^{2,5}]decan-*exo*-3-ol (**13a**). The latter compound served as precursor to both *syn*- and *anti*-tricyclo[4.2.1.1^{2,5}]-dec-3-enes. When pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-6,10-diol (**18**) was hydrogenated, the dihydro derivative **19a** resulted. By a sequence of reactions involving mesylation, displacement by iodide ion, and reductive deiodination, **19a** was transformed into *syn*-tricyclo[4.2.1.1^{2,5}]deca-3,7-diene (**1**). Warming of **1** to 55–80 °C promotes efficient Cope rearrangement to *cis,-syn,cis*-tricyclo[5.3.0.0^{2,6}]deca-3,8-diene (**3**). Lastly, the behavior of **4** under electrophilic and strongly acidic conditions is described. That neither the bromination of **4** nor its isomerization to adamantane can be effected readily is taken as an indication that this exceptionally highly strained molecule cannot ionize readily and transform itself into more thermodynamically stable cations capable of controlled Wagner–Meerwein shifts.

A thermally or photochemically excited polyolefinic molecule will almost invariably react with strict adherence to orbital symmetry control, because of the obvious energetic advantages to be gained by following such pathways. Cyclopentadiene is a case in point. While thermal association proceeds exclusively by [4 + 2]π cycloaddition to give *endo*-dicyclopentadiene, photochemical activation results only in intramolecular electronic reorganization and bicyclo[2.1.0]pentene formation.[1] Other possible dimerization reactions, such as those leading to the interesting tricyclic hydrocarbons **1–3**, are either disallowed on the basis of frontier orbital considerations or disfavored for entropic and steric reasons.


1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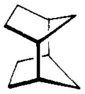
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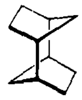
5

These molecules, and the related saturated hydrocarbons **4** and **5** as well, have attracted special interest for several reasons. As concerns **1–3**, knowledge of the relative levels of through-bond and through-space interaction would be revealing.[2,3] All three are considered to be reasonably rigid structures containing two π systems capable of effective through-bond interaction with resultant significant lengthening of these particular σ bonds on the molecular periphery. In contrast, while **1** and **3** might exhibit through-space coupling, **2** cannot possibly partake of this phenomenon because of obvious geometric constraints. At the same time, **1–3** are not anticipated to be capable of facile thermal fragmentation to cyclopentadiene. The energies required to achieve the necessary [4 + 4] and [2 + 2] cycloreversions could, on the other hand, provide quantitative indication of the "forbiddenness" of such reactions.

The $C_{10}H_{16}$ isomers **4** and **5** not only have comparable topological appeal, but also enjoy an isomeric relationship to adamantane. Molecular mechanics calculations have assessed **4** to be a highly strained substance, chiefly because the 1,3 fusion of two cyclopentane rings in "head-to-head" fashion leads to full eclipsing of all the endo hydrogens.[4] Steric strain is lowered in the "head-to-tail" orientation adopted by **5** as the direct result of the more staggered arrangement of the interior methylene hydrogens. Therefore, this pair of isomers could provide an estimate of the steric forces which gain importance as one five-membered ring is rotated by $\pi/5$ radians above a second while being maintained within bonding promixity. Also, the Lewis acid catalyzed isomerizations of **4** and **5** are anticipated to hold considerable mechanistic interest.[5] On the basis of molecular mechanics calculations, both **4** and **5** have been ignominiously relegated to mechanistic dead-end positions in "adamantaneland".

Clearly, the successful preparation of such molecules rests upon suitable improvisation of indirect synthetic methodology. In this paper, we report details of the relatively efficient preparation of **1** and **3–5**. Since the appearance of our preliminary communications on this subject,[7,8] Eaton and Ganter have published their independent work describing complementary alternative approaches to *syn*- and *anti*-tricyclo[4.2.1.1^{2,5}]decane (**4** and **5**).[9,10] Additionally, Turro and co-workers have recently gained access to **3** by suitable decomposition of an appropriate azo precursor molecule.[11]

syn-Tricyclo[4.2.1.1^{2,5}]decane (**4**). The face-to-face juxtapositioning of two cyclopentane rings which forms the struc-

0002-7863/79/1501-7599$01.00/0