

hydrogen transfer and those for deuterium transfer, without invoking a breakdown of the Born-Oppenheimer approximation.

Acknowledgment. The work of M.M.K. and D.O. was supported in part by the National Science Foundation through Grant No. CHE85-15014, that of D.G.T. was supported in part by the

U.S. Department of Energy through Contract No. DE-AC02-79ER10425, and that of B.C.G. was supported by the U.S. Army Research Office under Contract No. DAAG-29-84-C-0011.

Registry No. 1a, 84811-85-8; 1b, 47072-02-6; 1c, 102808-44-6; 1d, 89321-40-4; 1e, 85289-84-5; 1f, 89321-43-7; D₂, 7782-39-0.

Isotope Effects in Double Proton Transfer Reactions

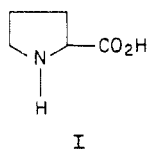
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Kinetic isotope effects are calculated for a reaction involving the simultaneous transfer of two protons. A linear transition state of two protons between three heavy entities of equal mass is assumed. Expressions are obtained for the four frequencies associated with motion along the line of centers. The variation in the size of these frequencies and their associated amplitudes as a function of the coupling of the protonic motion is explored. As the coupling is increased, one finds possible transition states where the reaction coordinate involves heavy-atom motion rather than a protonic vibration; such a transition state could exhibit a kinetic isotope effect of 2 to 3. Kinetic isotope effects larger than 20 are unlikely. The breakdown of the rule of the geometric mean for successive deuterium substitutions is explored; the largest breakdown is found for a concerted symmetrical transition state and may be as large as 15%. The breakdown of the Swain-Schaad relation is smaller; for a symmetrical transition state it may be 5%.

Introduction

In reactions that involve the transfer of two protons, an interesting question is whether there are two protons in flight in a single transition state or there are two successive transition states in which each proton is transferred one at a time. Examples of this type of system are numerous and range from classical reactions such as the enolization of acetone¹ and proton motion in the aqueous solvent,² through transfers in cyclical systems investigated by Limbach,^{3,4} to transfers in biochemical systems⁵ and in particular in enzyme-catalyzed reactions. An example of such an enzyme-catalyzed reaction is the racemization of proline (I)



catalyzed by the enzyme proline racemase. We have recently established the complete mechanism and free energy profile for this reaction.⁶ In order to answer the question posed above, we compared the kinetic isotope effect by substituting D for H on the first (α) site with H on the second (β) site with the kinetic isotope effect from the same substitution of D for H on the α site but this time with D on the β site;^{7,8} we compared $k_{D,H}/k_{H,H}$ with $k_{D,D}/k_{H,D}$. For a single concerted transition state, where the rule of the geometric mean⁹ is obeyed, we would expect that these two isotope effects would be the same. On the other hand, for two consecutive transition states the substitution of D for H on the β site changes the relative free energies of the two transition states

so that the isotope effect observed for substitution on the α site will not be the same in the two cases. We have described elsewhere the detailed methodology of this approach.⁸ This method was also devised independently by Cleland and his group and applied by them to a number of enzyme-catalyzed reactions.¹⁰⁻¹² However, the success of the method for double-proton transfers depends on whether the rule of the geometric mean holds for the successive substitutions in the single concerted transition state. In this paper we explore this question.

Another approach to the same problem, proposed by Northrop,¹³ is to use the breakdown of the Swain-Schaad relation.¹⁴ The Swain-Schaad relation relates the tritium and deuterium isotope effects:

$$k_D/k_H = (k_T/k_H)^{1.44}$$

Northrop argued that for a single transition state the relationship should be obeyed, while for two concerted transition states there would be a breakdown in the relation because again the contributions of the two partially rate limiting transition states would be different for the deuterium and for the tritium substitution. We have argued that the deviations are small and therefore the method requires data of the highest precision.¹⁵ In this paper we explore the breakdown of the Swain-Schaad relation which arises in a single transition state from the coupled motion of the two protons.

The third question that we address is the size of the isotope effect to be expected in a single concerted transition state. This has been a point of controversy for some time.^{16,17} One might argue that because two protons have lost their zero point energy and are flying in the transition state one would expect a larger

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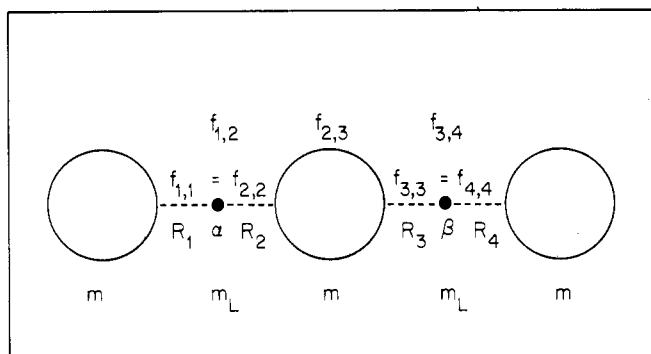


Figure 1. Model for the transition state showing the α and β protonic sites and the force constants.

isotope effect than when just one proton is involved. The counter argument, advanced by Kreevoy, is that in the transition state only one vibration has become a reaction coordinate; the other real vibration has a countervailing difference in zero point energy and hence the isotope effect is normal. We shall show that depending on the force constants in the transition state both cases can be found.

In addition an interesting third case can be found in which neither proton is flying but the reaction coordinate involves movement of the heavy atoms. This type of transition state is similar to that originally proposed by Kreevoy.¹⁸ We shall delineate the conditions for the force constants that give rise to these different types of transition state.

Recently Limbach discussed the differential effects of tunneling on the isotope effects observed in these systems.^{3,4} Although tunneling is established in his particular system, it is not a universal feature of proton transfers and still is the exception rather than the rule. In order not to make our treatment too complicated and in order to focus on the effects of the coupling of the different vibrations, we will ignore any tunneling effects. For the same reasons, we deal with a simplified system. The purpose of this paper is to obtain insight into these systems by understanding a simplified system in detail rather than wallowing in computer calculations. We shall use the approach of Westheimer,¹⁹ Bell,²⁰ and Albery²¹ in their discussion of the similar problems involved in a single-proton transfer.

Model

We assume a linear system consisting of two protons sandwiched between three more massive entities as shown in Figure 1. In order to reduce the number of parameters to a manageable number we assume that the masses of the larger entities are all identical and equal to m . We further make the reasonable assumption that m is much larger than the mass of the protonic species, designated m_L where as usual L can be H, D, or T. The internal coordinates R_1 , R_2 , R_3 , and R_4 describe the interatomic distances, and the atoms are positioned along the x coordinate from x_1 to x_5 as shown in Figure 1. The force constants are also shown. Again for simplicity we have assumed that the protons are symmetrically placed and that $f_{1,1} = f_{2,2}$ and $f_{3,3} = f_{4,4}$.

Basic Equations

The variation of the potential energy, U , is given by

$$\Delta U = \frac{1}{2}f_{1,1}(R_1^2 + R_2^2) + f_{1,2}R_1R_2 + \frac{1}{2}f_{2,2}(R_3^2 + R_4^2) + f_{3,4}R_3R_4 + f_{2,3}R_2R_3 \quad (1)$$

The first three terms on the right-hand side of eq 1 describe the bonding of the first proton and are the same as used in the Westheimer treatment.¹⁹ The next three terms similarly describe the bonding of the second proton. The final term describes the coupling of the two systems. If $f_{2,3}$ is zero, then we have two

TABLE I: Coefficients in Equation 11

m	n			
	1	2	3	4
1	$-(2 + \gamma_\alpha + \gamma_\beta)$	$-(2 + \gamma_\beta)$	$-(1 + \gamma_\beta)$	-1
2	1	$-(2 + \gamma_\beta)$	$-(1 + \gamma_\beta)$	-1
3	1	$1 + \gamma_\alpha$	$-(1 + \gamma_\beta)$	-1
4	1	$1 + \gamma_\alpha$	$2 + \gamma_\alpha$	-1
5	1	$1 + \gamma_\alpha$	$2 + \gamma_\alpha$	$2 + \gamma_\alpha + \gamma_\beta$

independent protonic systems. The larger is $f_{2,3}$, the stronger is the coupling of the two subsystems.

We now normalize the force constants with $f_{2,3}$ and define the following dimensionless parameters:

$$\alpha = f_{1,1}/f_{2,3} \quad (2)$$

$$\alpha' = f_{1,2}/f_{2,3} \quad (3)$$

$$\beta' = f_{3,4}/f_{2,3} \quad (4)$$

$$\beta = f_{4,4}/f_{2,3} \quad (5)$$

The kinetic energy, T , is given by

$$T/(\frac{1}{2}m) = \dot{x}_1^2 + \gamma_\alpha \dot{x}_2^2 + \dot{x}_3^2 + \gamma_\beta \dot{x}_4^2 + \dot{x}_5^2 \quad (6)$$

where for both the α and β sites

$$\gamma = m_L/m \quad (7)$$

Following the normal procedure,²² in the Langevin equation we need expressions for $(1/m)(\partial T/\partial R_n)$, where

$$\frac{1}{m} \frac{\partial T}{\partial R_n} = \dot{x}_1 \frac{\partial \dot{x}_1}{\partial R_n} + \gamma_\alpha \dot{x}_2 \frac{\partial \dot{x}_2}{\partial R_n} + \dot{x}_3 \frac{\partial \dot{x}_3}{\partial R_n} + \gamma_\beta \dot{x}_4 \frac{\partial \dot{x}_4}{\partial R_n} + \dot{x}_5 \frac{\partial \dot{x}_5}{\partial R_n} \quad (8)$$

The internal coordinates R are related to x by the following general relation:

$$\dot{R}_n = \dot{x}_{n+1} - \dot{x}_n \quad (9)$$

The conservation of momentum leads to

$$\dot{x}_1 + \gamma_\alpha \dot{x}_2 + \dot{x}_3 + \gamma_\beta \dot{x}_4 + \dot{x}_5 = 0 \quad (10)$$

From the four equations given by eq 9 and from eq 10 we obtain five relations for \dot{x}_n of the form

$$(3 + \gamma_\alpha + \gamma_\beta)\dot{x}_m = \sum B_n \dot{R}_n \quad (11)$$

where the coefficients B_n are collected in Table I.

Next we define a dimensionless function of the frequency, y :

$$y = 4\pi^2\nu^2 m/f_{2,3}(3 + \gamma_\alpha + \gamma_\beta)^2 \quad (12)$$

Substitution from the five different expressions for x_n given by eq 11 and Table I in the four different expressions given by eq 8 gives the following four expressions relating the frequency function, y , and the amplitudes A_1 – A_4 associated with motion involving R_1 – R_4

$$A_1(C_{1,1} - \alpha/y) + A_2(C_{1,2} - \alpha'/y) + A_3C_{1,3} + A_4C_{1,4} = 0 \quad (13)$$

$$A_1(C_{2,1} - \alpha'/y) + A_2(C_{2,2} - \alpha/y) + A_3(C_{2,3} - 1/y) + A_4C_{2,4} = 0 \quad (14)$$

$$A_1C_{3,1} + A_2(C_{3,2} - 1/y) + A_3(C_{3,3} - \beta/y) + A_4(C_{3,4} - \beta'/y) = 0 \quad (15)$$

$$A_1C_{4,1} + A_2C_{4,2} + A_3(C_{4,3} - \beta'/y) + A_4(C_{4,4} - \beta/y) = 0 \quad (16)$$

where the coefficients $C_{m,n}$ are collected in Table II. In deriving these expressions we have neglected γ^2 terms, because γ is much smaller than one.

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TABLE II: Coefficients $C_{m,n}$ in Equations 13–16

m	n			
	1	2	3	4
1	$6 + 5c\alpha + 5c\beta$	$6 + 2c\alpha + 5c\beta$	$3 + c\alpha + 4c\beta$	$3 + c\alpha + c\beta$
2	$6 + 2c\alpha + 5c\beta$	$6 + 8c\alpha + 5c\beta$	$3 + 4c\alpha + 4c\beta$	$3 + 4c\alpha + c\beta$
3	$3 + c\alpha + 4c\beta$	$3 + 4c\alpha + 4c\beta$	$6 + 5c\alpha + 8c\beta$	$6 + 5c\alpha + 2c\beta$
4	$3 + c\alpha + c\beta$	$3 + 4c\alpha + c\beta$	$6 + 5c\alpha + 2c\beta$	$6 + 5c\alpha + 5c\beta$

Now multiplication of eq 13 by $(1 + \gamma_\alpha)$ followed by subtraction of eq 14 gives (neglecting γ^2 terms)

$$A_1 = (\alpha_\Delta A_2 + A_3)/(\alpha_\Delta - 9\gamma_\alpha y) \quad (17)$$

where

$$\alpha_\Delta = \alpha - \alpha' \quad (18)$$

Similarly, multiplication of eq 16 by $(1 + \gamma_\beta)$ and subtraction of eq 15 gives

$$A_4 = (\beta_\Delta A_3 + A_2)/(\beta_\Delta - 9\gamma_\beta y) \quad (19)$$

where

$$\beta_\Delta = \beta - \beta' \quad (20)$$

Substitution of eq 17 and 19 in eq 13 and 16 gives the following two symmetrical equations:

$$\left[\frac{\alpha_\Delta(6 - \alpha/y)}{\alpha_\Delta - 9\gamma_\alpha y} + 6 - \frac{\alpha'}{y} + \frac{3}{\beta_\Delta - 9\gamma_\beta y} \right] A_2 = - \left[\frac{6 - \alpha/y}{\alpha_\Delta - 9\gamma_\alpha y} + 3 + \frac{3\beta_\Delta}{\beta_\Delta - 9\gamma_\beta y} \right] A_3 \quad (21)$$

$$\left[\frac{\beta_\Delta(6 - \beta/y)}{\beta_\Delta - 9\gamma_\beta y} + 6 - \frac{\beta'}{y} + \frac{3}{\alpha_\Delta - 9\gamma_\alpha y} \right] A_3 = - \left[\frac{6 - \beta/y}{\beta_\Delta - 9\gamma_\beta y} + 3 + \frac{3\alpha_\Delta}{\alpha_\Delta - 9\gamma_\alpha y} \right] A_2 \quad (22)$$

Multiplication of eq 21 and 22 gives a quartic in y . The four roots to this quartic describe the four frequencies associated with the four stretching motions along the line of centers (see Figure 1). Substitution of the appropriate values of y in eq 17, 19, and either 21 or 22 gives the ratios of the amplitude factors for each vibration.

All-Hydrogen System

We start by considering the all-hydrogen system. Then in eq 21 and 22, γ_α and γ_β will both be equal to m_H/m , and we write

$$w = 9\gamma_H y = 4\pi^2 \nu^2 m_H / k_{2,3} \quad (23)$$

where $\gamma_H = m_H/m$ and where in eq 12 we have ignored the small γ_H terms with respect to 3. Substitution of eq 23 in eq 21 and 22 then gives the following quartic for the frequency function w

$$w^4 - 2w^3(\alpha_\Delta + \beta_\Delta) + w^2[4\alpha_\Delta\beta_\Delta - 1 + 2\gamma_H[(\alpha_\Delta + \beta_\Delta) \times (\alpha_\Sigma + \beta_\Sigma - 1) - 2\alpha_\Delta\beta_\Delta]] - w\gamma_H[(4\alpha_\Delta\beta_\Delta - 1)(\alpha_\Sigma + \beta_\Sigma) - \alpha_\Delta - \beta_\Delta - 2\alpha_\Delta\beta_\Delta] + 3\gamma_H^2[\alpha_\Delta\beta_\Delta\alpha_\Sigma\beta_\Sigma - \alpha\beta] = 0 \quad (24)$$

where

$$\alpha_\Sigma = \alpha + \alpha' \quad (25)$$

$$\beta_\Sigma = \beta + \beta' \quad (26)$$

and as before small γ_H terms have been neglected.

Now for most values of the force constants eq 24 can be separated into two quadratic equations. First when $w \sim \alpha$ etc. \sim or > 1 , then the γ_H terms in eq 24 can be neglected and, dividing by w^2 , we obtain the following quadratic equation:

$$w^2 - 2w(\alpha_\Delta + \beta_\Delta) + 4\alpha_\Delta\beta_\Delta - 1 = 0 \quad (27)$$

The roots to this equation are

$$w_{H,H} = \alpha_\Delta + \beta_\Delta \pm [(\alpha_\Delta - \beta_\Delta)^2 + 1]^{1/2} \quad (28)$$

The subscript H,H reminds us that we are considering the all-H system.

The second quadratic equation we obtain from eq 24 describes lower frequencies where $w \sim \gamma_H$. Inspection then shows that the w^4 and w^3 terms can be neglected to give

$$(w/\gamma_H)^2(4\alpha_\Delta\beta_\Delta - 1) - (w/\gamma_H)[(4\alpha_\Delta\beta_\Delta - 1) \times (\alpha_\Sigma + \beta_\Sigma) - \alpha_\Delta - \beta_\Delta - 2\alpha_\Delta\beta_\Delta] + 3(\alpha_\Delta\beta_\Delta\alpha_\Sigma\beta_\Sigma - \alpha\beta) = 0 \quad (29)$$

From eq 23 and 28 the two high-frequency roots depend on m_H but not on the heavy mass m , while, from eq 23 and eq 29, the two low-frequency roots depend on m and not on m_H . Thus the two high-frequency roots describe the vibrations of the H atoms, while the two low-frequency roots describe heavy-atom motion. The values of the two low frequencies are insensitive to isotopic substitution.

The separation of eq 24 into the two quadratic equations, eq 27 and 29, is valid as long as

$$4\alpha_\Delta\beta_\Delta \neq 1 \quad (30)$$

When $4\alpha_\Delta\beta_\Delta$ is close to unity, then according to eq 27 one of the high-frequency values tends to zero, while according to eq 29 one of the low-frequency roots tends to infinity! These paradoxical results arise because under these conditions the system is closely coupled and the separation is no longer valid. That is why we have retained the γ_H term in the w^2 term in eq 24, and we will consider this case in more detail below. But first we consider the hydrogenic vibrations described in eq 27 and 28.

Hydrogenic Vibrations

Under the conditions where eq 27 is a good approximation, eq 21, 22, and 27 can be replaced by the following much simpler expression:

$$A_3/A_2 = w - 2\alpha_\Delta = 1/(w - 2\beta_\Delta) \quad (31)$$

Substitution of eq 31 in eq 17 and 19 yields the following simple results:

$$A_1/A_2 = A_4/A_3 = -1 \quad (32)$$

The fact that $A_1 + A_2$ and $A_3 + A_4$ are constant shows that for the hydrogenic vibrations the relative positions of the three heavy entities remain unaltered.

Next we note from eq 28 that when

$$4\alpha_\Delta\beta_\Delta > 1 \quad (33)$$

both of the roots for w are positive. Under these conditions neither of the hydrogenic vibrations is a reaction coordinate. On the other hand, when

$$4\alpha_\Delta\beta_\Delta < 1 \quad (34)$$

then one of the roots for w is negative. From eq 23 we then obtain an imaginary value of the frequency. This corresponds with a hydrogenic vibration being the reaction coordinate in the transition state. The crucial boundary between two stable hydrogenic vibrations and a hydrogenic transition state is the condition

$$4\alpha_\Delta\beta_\Delta = 1 \quad (35)$$

(As discussed above, however, the treatment breaks down in the region of this boundary; see eq 30.)

From eq 28 and 31 we obtain the following results for A_3/A_2 :

$$A_3/A_2 = \beta_\Delta - \alpha_\Delta \pm [(\alpha_\Delta - \beta_\Delta)^2 + 1]^{1/2} \quad (36)$$

In Figure 2 we show how A_3/A_2 varies as a function of α_Δ and β_Δ ; the insets show the type of vibration that results. First, in the top right-hand corner, where both α_Δ and β_Δ are large, the coupling force constants, $f_{1,2}$, $f_{2,3}$, and $f_{3,4}$ are all small; here we find stable species with both roots to eq 27 being positive, corresponding to real vibrations.

Second, in the top left-hand and bottom right-hand corners of the diagram, where either $\alpha_\Delta \gg \beta_\Delta$ or $\beta_\Delta \gg \alpha_\Delta$, one proton is bound much more tightly than the other. We find that the positive root of eq 28 describes the real vibration of the more tightly bound proton. The negative root, on the other hand, may give a reaction

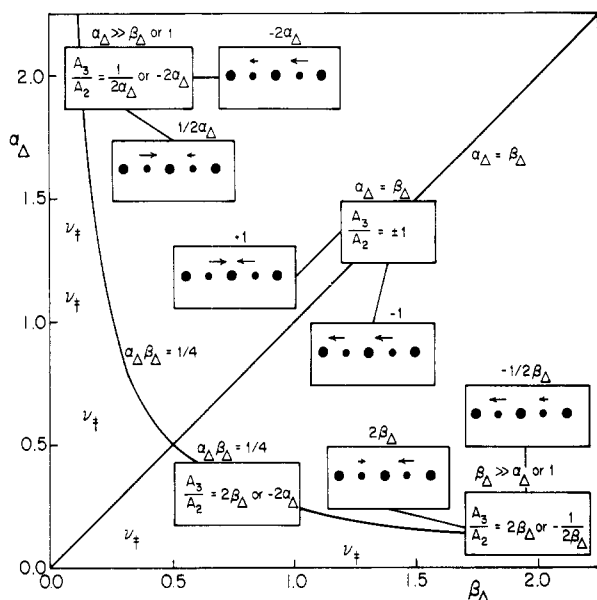


Figure 2. Variation of the amplitude ratio, A_3/A_2 (eq 36), for the hydrogenic vibrations. The insets show the different types of vibration. For $\alpha_\Delta \beta_\Delta > 1/4$ both hydrogenic vibrations are real; for $\alpha_\Delta \beta_\Delta < 1/4$ one hydrogenic vibration is the reaction coordinate.

coordinate if the condition of eq 34 holds; the reaction coordinate is the transfer of the less tightly bound proton. Under these conditions there is little coupling between the two protons and the transition state involves only a single proton transfer. In the middle of the diagram, where $\alpha_\Delta \sim \beta_\Delta$, we find the most coupling. Now if there is a reaction coordinate, both protons are involved. For the particular case of $\alpha_\Delta = \beta_\Delta$ we find that $A_3 = -A_2$; that is, the distance between the two protons does not alter, and they are therefore moving with the same velocity.

Heavy-Atom Reaction Coordinate

It might be thought from the above discussion that the condition $4\alpha_\Delta \beta_\Delta < 1$, given by eq 34, would have to be fulfilled before we had a transition state with an imaginary frequency. In fact, this is not the case. The reaction coordinate can consist of heavy-atom motion described by a negative root to eq 29 rather than eq 27. Returning to the full quartic expression, eq 24, the boundary between stable species with all four roots positive and transition states with three positive roots and one negative is given by $w = 0$. This arises when the last term, the w^0 term, in eq 24 is zero; this condition may be written

$$\alpha_\Delta \beta_\Delta = 1 / [(1 + \alpha' / \alpha)(1 + \beta' / \beta)] > 1/4 \quad (37)$$

The inequality arises because we assume that α' and β' are smaller than α and β , respectively; this is equivalent to assuming that α_Δ and β_Δ are both positive. The condition in eq 37 is therefore fulfilled at a larger value of $\alpha_\Delta \beta_\Delta$ than is the condition in eq 35 where $\alpha_\Delta \beta_\Delta = 1/4$. Hence, in general, a region where there is a heavy-atom reaction coordinate lies between the region of stable molecules and the region where there is a transition state with a hydrogenic reaction coordinate. If one assumes that for a coupled system $f_{2,3}$ is the most important coupling force constant, then an approximate locus for the dividing line between stable species and transition states is $\alpha_\Delta \beta_\Delta = 1$. On the other hand, if $f_{2,3}$ is insignificant, then α_Δ and β_Δ will be very large and can only be reduced by matching α and α' and β and β' . Under these conditions the region of the heavy-atom reaction coordinate vanishes.

Turning to the amplitude factors, we find for $w = 0$ from eq 17, 19, 21, and 22 the following results:

$$A_3/A_2 = -(\alpha_\Delta)^2/\alpha = -\beta/(\beta_\Delta)^2 = -(\beta/\alpha)^{1/2}(\alpha_\Delta/\beta_\Delta) \quad (38)$$

$$A_1/A_2 = -\alpha'/\alpha \quad (39)$$

$$A_4/A_3 = -\beta'/\beta \quad (40)$$

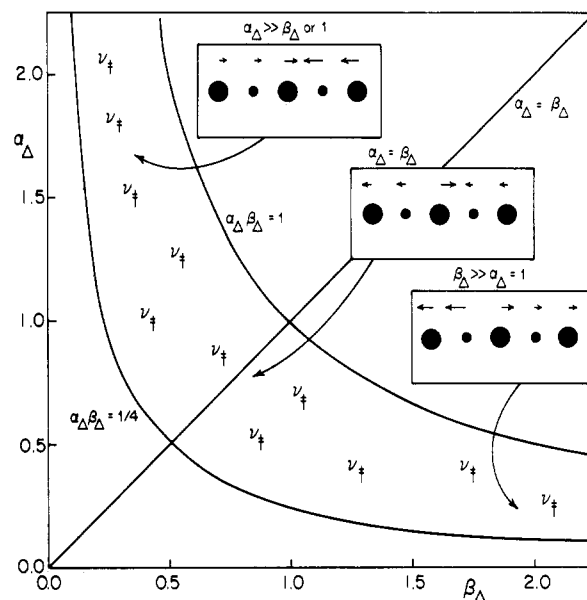


Figure 3. Variation of the amplitude ratios for the heavy-particle vibrations with α_Δ and β_Δ for the particular case when $w = 0$ (eq 38-40). The insets show the different types of vibration.

Since α' and β' are likely to be smaller than α and β , respectively, eq 39 and 40 show that most of the motion in the reaction coordinate is in A_2 and A_3 . Figure 3 illustrates the different types of vibration. For the unsymmetrical cases in the top left-hand corner and bottom right-hand corner, we find that the principal motion is a translation of the heavy particle and the less stable proton with respect to the remaining two heavy entities and the more stable proton. This situation is reminiscent of a similar type of reaction coordinate found for an unsymmetrical single proton transfer.²¹ For the symmetrical case the motion is a coupled translation of the two outer particles and their protons with respect to the central particle. Remember that under these conditions both hydrogenic vibrations are real and each will have a substantial zero point energy difference.

The $4\alpha_\Delta \beta_\Delta = 1$ Case

As discussed above, the separation of the quartic equation (eq 24) into the two quadratic equations (eq 27 and 29) is no longer valid when $4\alpha_\Delta \beta_\Delta = 1$. Instead we have to use the full quartic. We find from the w^4 and w^3 terms that there is one real hydrogenic vibration with

$$w = 2(\alpha_\Delta + \beta_\Delta)$$

Similarly, from the w term and the negative w^0 terms we can find one real heavy-atom vibration with

$$w = \gamma_H(\alpha\beta - \alpha_\Delta \beta_\Delta \alpha_2 \beta_2) / (\alpha_\Delta + \beta_\Delta + 2\alpha_\Delta \beta_\Delta)$$

(The w^0 term is negative because, as discussed above, $\alpha_\Delta \beta_\Delta$ will be smaller than the $w = 0$ condition.) The remaining two vibrations are given by the w^3 and w terms, which are of order $(\gamma_H)^{3/2}$:

$$w = \pm(\gamma_H)^{1/2} [1/2 + \alpha_\Delta \beta_\Delta / (\alpha_\Delta + \beta_\Delta)]^{1/2} \quad (41)$$

Substitution of eq 41 in eq 24 shows that the other terms are of the order of $(\gamma_H)^2$ and hence can be neglected. The results in eq 41 show that the frequency function is now intermediate between the hydrogenic value (~ 1) and the heavy-atom value ($\sim \gamma_H$). The value of $\gamma_H^{1/2}$ is indeed small on the hydrogenic scale, where the approximate eq 27 gives zero, and large on the heavy-atom scale, where the approximate eq 29 gives infinity.

As regards the amplitude factors, we find from eq 17, 19, 21, and 22 that

$$A_3/A_2 = -2\alpha_\Delta = -1/(2\beta_\Delta) = -(\alpha_\Delta/\beta_\Delta)^{1/2} \quad (42)$$

and

$$A_1/A_2 = A_4/A_3 = -1 \quad (43)$$

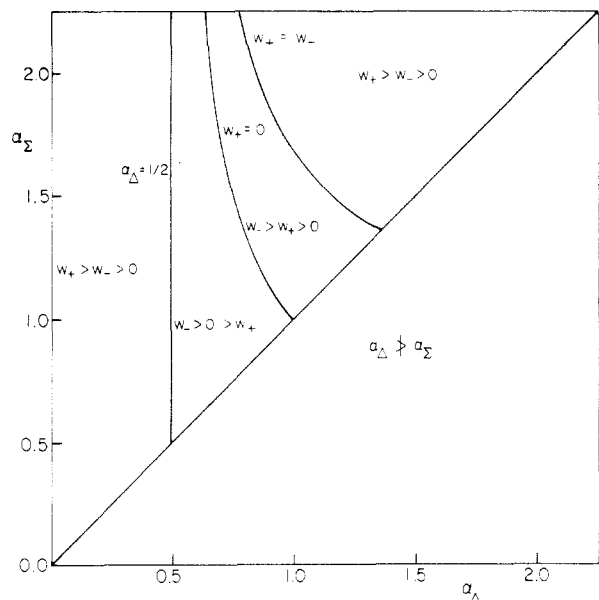


Figure 4. Diagram for the different cases for the heavy-particle motion showing the crossover condition where $w_+ = w_-$ (eq 47), the $w = 0$ condition (eq 45), and the intermediate case ($\alpha_\Delta = 1/2$). When the value of α_Δ crosses $1/2$, w_+ changes from being a negative reaction coordinate into a real vibration where $w_+ > w_-$.

Comparison of these results with those in eq 32 and 36 for the hydrogenic vibrations shows that the motion in the reaction coordinate is very similar to that in the hydrogenic case. It is interesting that eq 42 applies to both the positive and negative roots of eq 41. In both cases A_3/A_2 is negative, while for the hydrogenic vibrations A_3/A_2 is negative for the reaction coordinate but positive for the stable vibration. These characteristics of the different vibrations and how they change as the coupling constants increase, transforming a stable molecule into either a heavy particle or a hydrogenic transition state, will now be explored. For simplicity we will consider the totally symmetrical case where $\alpha = \beta$ and $\alpha' = \beta'$. This case is of more interest than the unsymmetrical cases where each proton transfer can be treated individually.

Amplitude Factors in the Symmetrical Case

Multiplication of eq 21 by eq 22, followed by substitution of all β by α , leads to an expression for the symmetrical case, where one can take the square root of either side and hence conclude directly that

$$A_3/A_2 = \pm 1 \quad (44)$$

(It is satisfactory that eq 36, 38, and 42 all reduce to eq 44 for the symmetrical case.) We can also obtain the following results for the frequencies of the heavy-atom motion, by taking first the positive sign and second the negative sign on taking the square root:

positive sign

$$A_3/A_2 = -1$$

$$w_+ = 3\gamma_H(\alpha_\Delta\alpha_\Sigma - \alpha)/(2\alpha_\Delta - 1) \quad (45)$$

negative sign

$$A_3/A_2 = +1$$

$$w_- = \gamma_H(\alpha_\Delta\alpha_\Sigma + \alpha)/(2\alpha_\Delta + 1) \quad (46)$$

Inspection shows that for a stable species, where α_Δ is large, because of the factor of 3 $w_+ > w_-$. However, because of the minus sign in the numerator, as the coupling constants increase it is w_+ that goes to zero and becomes a transition-state reaction coordinate. This is sensible since the type of motion that we want for the double-proton-transfer requires A_3/A_2 to be negative rather

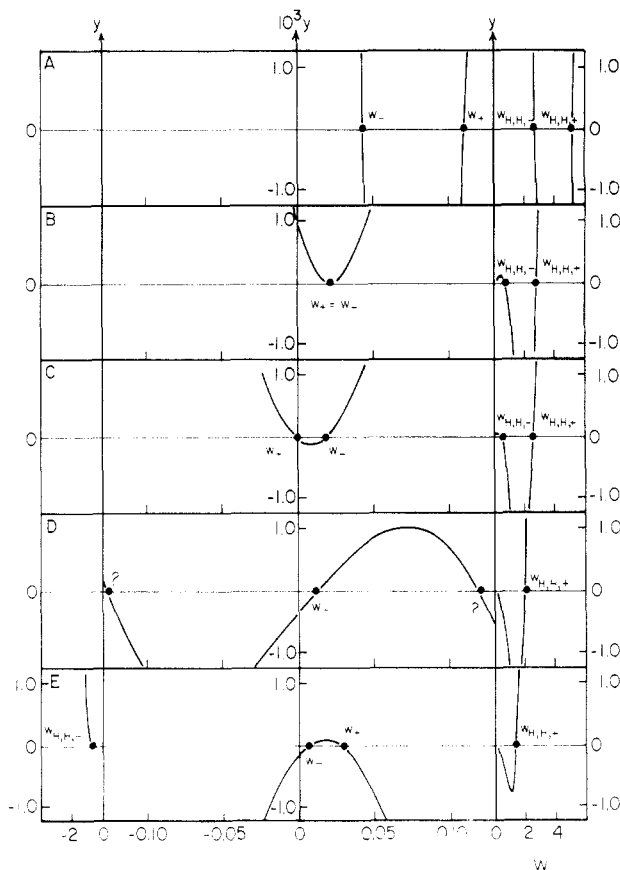


Figure 5. Plots of the quartic equation (eq 24) for the symmetrical case and for $\alpha = 3\alpha'$. Values of α_Δ are as follows: (A) $\alpha_\Delta = 2$, a stable species; (B) $\alpha_\Delta = 0.91$, the crossover condition; (C) $\alpha_\Delta = 0.75$, the $w = 0$ condition; (D) $\alpha_\Delta = 0.5$, the intermediate case; (E) $\alpha_\Delta = 0.25$, a hydrogenic transition state.

than positive. There is therefore a "crossover" point where $w_+ = w_-$. From eq 45 and 46 this occurs when

$$\alpha_\Sigma = (4\alpha_\Delta^2 + \alpha_\Delta)/(4\alpha_\Delta^2 - 1) \quad (47)$$

In Figure 4 we show the locus of the crossover condition, the $w = 0$ condition from eq 45, and the intermediate case, discussed above, when $4\alpha_\Delta\alpha_\Sigma = 1$ or $\alpha_\Delta = 1/2$. As one passes through the intermediate region the denominator in eq 45 changes sign and w_+ changes from being a reaction coordinate into a real heavy-particle vibration again. The reaction coordinate is then the hydrogenic vibration with $A_3/A_2 = -1$.

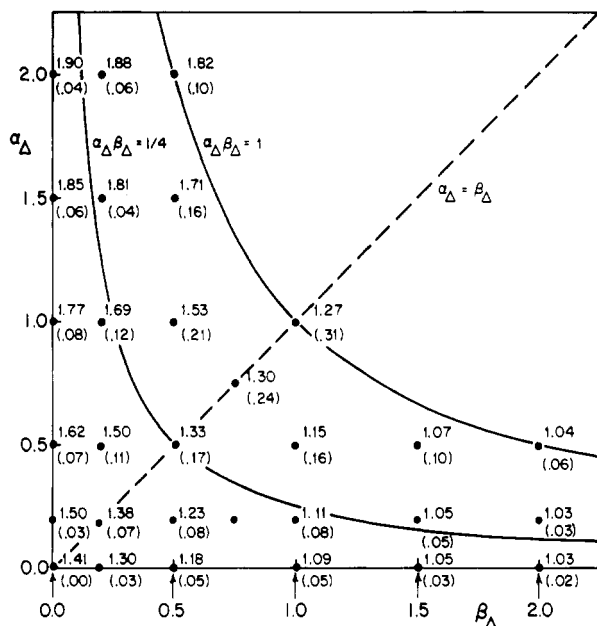
In Figure 5 we show a number of plots of the quartic equation for a particular case where we have taken $\alpha = 3\alpha'$; the plots show a stable species, the crossover case, the $w = 0$ condition, the intermediate $\alpha_\Delta = 1/2$ case, and a hydrogenic transition state. It can be seen that the roots corresponding to the $A_3/A_2 = +1$ vibrations do nothing surprising; the frequency of these real vibrations simply decreases as coupling increases. All the fun is in the vibrations with $A_3/A_2 = -1$. The second lowest root to the quartic for stable species starts as a real heavy-atom vibration, crosses the lowest root, develops into the heavy-atom reaction coordinate and then, passing through the intermediate region, finally becomes the hydrogenic reaction coordinate. In the intermediate region the stable hydrogenic $A_3/A_2 = -1$ vibration changes into the stable w_- heavy-particle vibration. These conclusions are summarized in Table III.

Ratios $w_{H,H}/w_{D,H}$ and $w_{H,D}/w_{D,D}$

We can now explore the size of the isotope effect as a function of the force constants in the transition state. We start by calculating the ratios $w_{H,H}/w_{D,H}$ and $w_{H,D}/w_{D,D}$ for the hydrogenic vibrations given by eq 28. Each w ratio describes the ratio of the square of the frequencies when D is substituted for H on the α site with either H or D on the β site. The ratios are calculated

TABLE III: Summary of Vibrational Characteristics for the Symmetrical Case

stable species	lowest root	second lowest root	second highest root	highest root
	heavy-particle vibrations		hydrogenic vibrations	
A_3/A_2 crossover	+1	-1	-1	+1
A_3/A_2	-1	+1	-1	+1
$w = 0$
transition states	ν_t
$\alpha_\Delta = 1/2$
	heavy-particle vibrations		H vibration	
A_3/A_2	-1	+1	-1	+1

**Figure 6.** Values of the ratio $w_{H,H,+}/w_{D,H,+} = (\nu_{H,H,+}/\nu_{D,H,+})^2$ for the positive root to eq 27 displayed as a function of α_Δ and β_Δ . The numbers in parentheses give values of D (eq 51), where D measures the difference in the ratio with deuterium as opposed to hydrogen on site β .

for both the positive ($A_3/A_2 = 1$) and the negative ($A_3/A_2 = -1$) roots given by eq 28 for the H,H system. From eq 24 we find the following results for the deuterated systems:

$$w_{D,H} = \frac{1}{2} \{ \alpha_\Delta + 2\beta_\Delta \pm [(\alpha_\Delta - 2\beta_\Delta)^2 + 2]^{1/2} \} \quad (48)$$

$$w_{H,D} = \frac{1}{2} \{ 2\alpha_\Delta + \beta_\Delta \pm [(2\alpha_\Delta - \beta_\Delta)^2 + 2]^{1/2} \} \quad (49)$$

$$w_{D,D} = \frac{1}{2} w_{H,H} \quad (50)$$

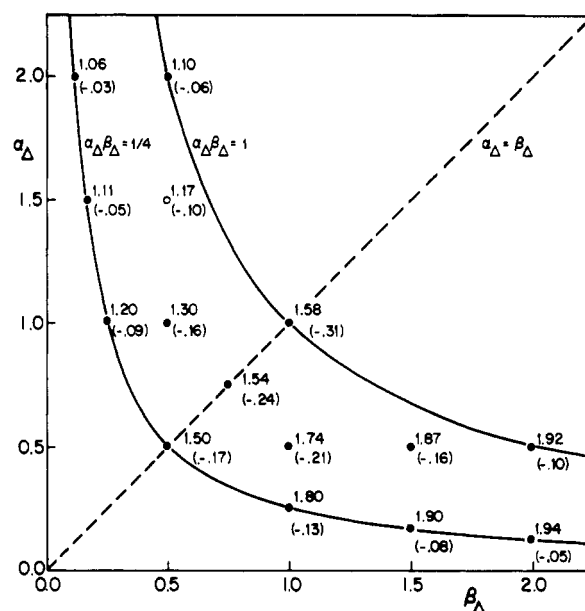
Taking the positive roots, results for the ratio $w_{H,H}/w_{D,H}$ are displayed in Figure 6. It can be seen that in the top left-hand corner the ratio tends toward 2, which is the value to be expected for the stable stretching motion of the tightly bound α proton (see Figure 2). In the bottom right-hand corner the ratio tends to unity. This is because in this corner the vibration is mainly the stretching motion of the tightly bound β proton and so will be little affected by deuterium substitution on the α site.

We also display in parentheses the difference, D , between the two ratios:

$$D = (w_{H,D}/w_{D,D}) - (w_{H,H}/w_{D,H}) \quad (51)$$

The reason why D is positive will be discussed below.

Turning to the negative roots of eq 28 and 48–50, we display similar results for the ratio $w_{H,H}/w_{D,H}$ and D in Figure 7. In this case the results are bound by the $4\alpha_\Delta\beta_\Delta = 1$ curve, where the vibration turns into a reaction coordinate. The values along this

**Figure 7.** Values of the ratio $w_{H,H,-}/w_{D,H,-} = (\nu_{H,H,-}/\nu_{D,H,-})^2$ for the negative root of eq 27 displayed as a function of α_Δ and β_Δ . The numbers in parentheses give values of D (eq 51). The diagram is bound by the hyperbola $\alpha_\Delta\beta_\Delta = 1/4$, where the negative root becomes the reaction coordinate. Along this hyperbola the same results are obtained from the quadratic equation (eq 27) and from considering the intermediate case.**TABLE IV: Summary of Vibrational Characteristics for a Symmetrical Stable Species**

isotopes	positive root	negative root
H, H		
$w =$	$2\alpha_\Delta + 1$	$2\alpha_\Delta - 1$
$A_3/A_2 =$	+1	-1
D, H and H, D		
$w =$	$2\alpha_\Delta$	α_Δ
D, H		
A_3/A_2	$\gg 1$	~ -0
H, D		
A_3/A_2	$\sim +0$	$\ll -1$
D, D		
$w =$	$\alpha_\Delta + 1/2$	$\alpha_\Delta - 1/2$
$A_3/A_2 =$	+1	-1

curve can be found by considering the w^3 and w terms from eq 24, as was done in the derivation of eq 41. We find

$$w_{H,H}/w_{D,H} = (\alpha_\Delta + 2\beta_\Delta)/(\alpha_\Delta + \beta_\Delta) \quad (52)$$

and

$$w_{H,D}/w_{D,D} = 2(\alpha_\Delta + \beta_\Delta)/(2\alpha_\Delta + \beta_\Delta) \quad (53)$$

It is very satisfactory that exactly the same results are found if one substitutes $\alpha_\Delta\beta_\Delta = 1/4 + \delta$ in eq 27 and the corresponding equations for the deuterated systems and then ignores the small w^2 terms. This means that in calculating the contribution to the isotope effect from this vibration we need only use the quadratic eq 27. The difference along $\alpha_\Delta\beta_\Delta = 1/4$ between $w = 0$ from eq 27 and the true value given by eq 41 will be unimportant since w is so small that its contribution to the overall isotope effect is negligible.

The pattern of the w ratio for the negative root (Figure 7) is complementary to that for the positive root. Now in the top left-hand corner the vibration describes the motion of the β proton and so is insensitive to isotopic substitution on the α site, while in the bottom right-hand corner the negative root describes the motion of the less stable α proton and so the ratio tends to its limiting value of 2.

We will now discuss why D is positive in Figure 6 for the positive root and negative in Figure 7 for the negative root. This is best done by considering the symmetrical case where $\alpha_\Delta = \beta_\Delta$. This case has also been discussed by Limbach.³ In Figure 8 we display

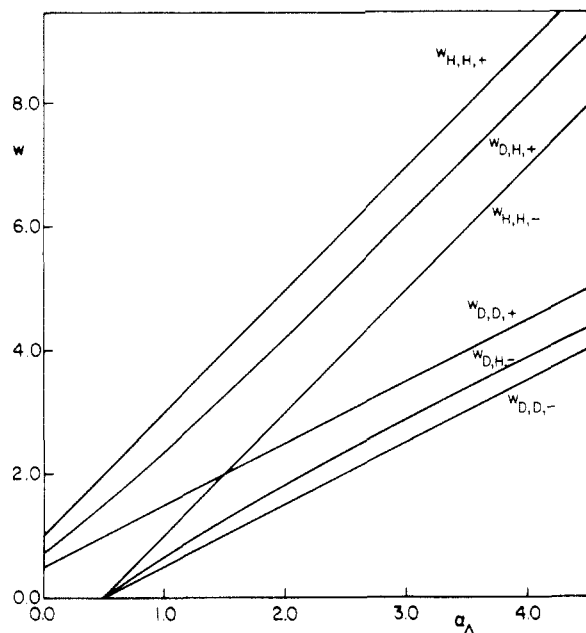


Figure 8. Variation of the different values of w (eq 28 and 48–50) with α_D for the symmetrical case ($\alpha_D = \beta_D$); for this case $w_{H,D,\pm} = w_{D,H,\pm}$.

how the different values of w , calculated from eq 28 and 48–50 vary with α_D along the $\alpha_D = \beta_D$ line in either Figures 6 or 7. When α_D is large, we have a stable molecule. Values of w and the corresponding amplitude factors are given in Table IV. It can be seen that, while the amplitude ratios for the H,H and D,D systems are ± 1 , for the singly deuterated systems the loss of isotopic symmetry means that there is no coupling of the motions; one vibration corresponds to the α stretch and the other to the β stretch. Substitution of one deuterium drops the frequency from the negative root but has little effect on the frequency from the positive root. Now if the rule of the geometric mean is to be obeyed and $D = 0$, then the singly deuterated value of w should be $2^{1/2}w_{D,D}$. Inspection of Figure 8 and Table IV shows that for the positive root this condition is only obeyed at $\alpha_D = 0$. Elsewhere the singly deuterated value lies closer to the H,H value and is larger than that predicted by the rule of the geometric mean. Larger values of $w_{D,H}$ or $w_{H,D}$ in eq 51 for D lead to D being positive. The opposite situation is found for the negative root. Here at large α_D the value of the singly deuterated w lies close to the D,D value and is less than that required by the rule of the geometric mean; hence eq 51 leads to negative values of D .

For the negative root an interesting situation arises at the point $\alpha_D = \beta_D = 1/2$, where all w tend to zero. For this particular case we find that the values of w are in the following ratios:

$$w_{H,H}:(w_{D,H} = w_{H,D}):w_{D,D} = \frac{1}{2}:\frac{1}{3}:\frac{1}{4}$$

The ratios arise from the total mass (2, 3, and 4) that is freely translating ($w = 0$) under these conditions.

Size of the Isotope Effect

Isotope effects can either be reported as ratios of rate constants (k_H/k_D) or as values of fractionation factors, φ , where²⁰

$$k_D/k_H = \prod \varphi_T / \prod \varphi_R \quad (54)$$

and φ_T and φ_R are the fractionation factors for sites in the transition state and reactants, respectively. For a two-site problem such as this the fractionation factor approach is preferred. However, it does suffer from one disadvantage. Those not skilled in the art of fractionation factors have a better understanding of the size of k_H/k_D ratios, which for this system are greater than one, as opposed to the size of φ s, which are smaller than one. For this paper we will therefore adopt the following compromise procedure. To simplify the notation we will first assume that all reactant fractionation factors are unity. Second, we will report results as

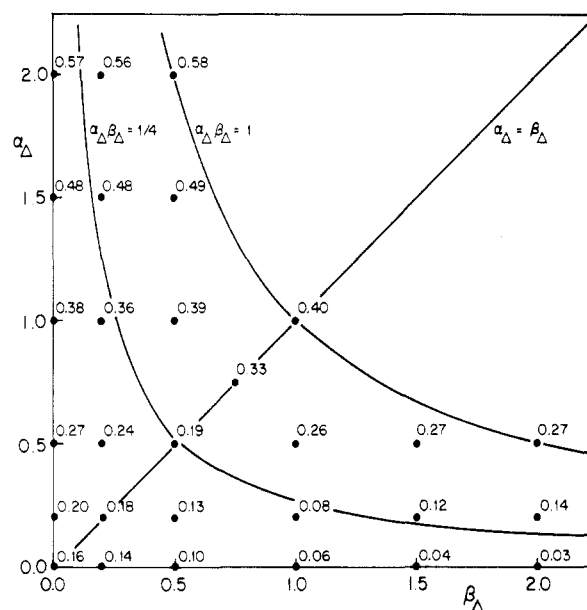


Figure 9. Values of $\sum w^{1/2}$ (eq 58) displayed as a function of α_D and β_D .

φ_T^{-1} , thereby using fractionation factors but reporting them so that they correspond to k_H/k_D .

The usual treatment of kinetic isotope effects²¹ then gives

$$\varphi_{T,D,H}^{-1} = 7^x \quad (55)$$

where²¹

$$x = 1 - [\theta^{1/2} / (2^{1/2} - 1)] \sum w^{1/2} \quad (56)$$

$$\theta = f_{2,3} / f_{1,1} \quad (57)$$

and

$$\sum w^{1/2} = w_{H,H,+}^{1/2} + w_{H,H,-}^{1/2} - w_{D,H,+}^{1/2} - w_{D,H,-}^{1/2} \quad (58)$$

with the sign of the root to eq 28 and 48 being indicated by the + and - subscripts. In deriving eq 56 we have assumed that $f_{1,1}$ in the reactant and transition state are the same. Our previous work²¹ shows that the results of calculations of this type are not too greatly affected by assumptions about the variation in $f_{1,1}$. The value of 7 in eq 55 is chosen as a reasonable value for the maximum isotope effect to be expected when there is no countervailing zero point energy difference in the transition state and $\sum w^{1/2} = 0.25$. From eq 55 to 58, we see that the observed isotope effect depends not only on the w ratios discussed above but also on the absolute size of the frequencies themselves. Besides the crucial force-constant parameters, α_D and β_D , which describe the hydrogenic vibrations, we also have to introduce the force-constant ratio θ , which compares the vital coupling force constant $f_{2,3}$ with the stretching force constant $f_{1,1}$.

From eq 55 to 58, the observed isotope effect depends on θ and on $\sum w^{1/2}$. Values of $\sum w^{1/2}$ are displayed in Figure 9. In keeping with Figure 6 the values are largest in the top left-hand corner and drop toward zero in the bottom right-hand corner. Figure 10 shows how the isotope effect for particular values of α_D and the corresponding value of $\sum w^{1/2}$ varies with θ . We also indicate the points for different values of α_D where $f_{1,1} = f_{2,3}$ and where $f_{1,2} = f_{2,3}$. In order to produce common curves, the x axis has been scaled by plotting $\alpha_D \theta$. From eq 2, 3, 18, and 57, $\alpha_D \theta < 1$ and, as shown in Figure 10, when $\alpha_D \theta = 1$, $f_{1,2} = 0$. From the results in Figures 9 and 10, together with the reasonable assumption that $f_{1,2} \sim f_{2,3}$, we obtain the approximate values for $\varphi_{T,D,H}^{-1}$ displayed in Figure 11. In the top left-hand corner the fractionation factor

(23) Kresge, A. J. *Pure Appl. Chem.* 1964, 8, 243.

(24) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: London, 1978; pp 77 ff.

(25) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: London, 1978; p 90.

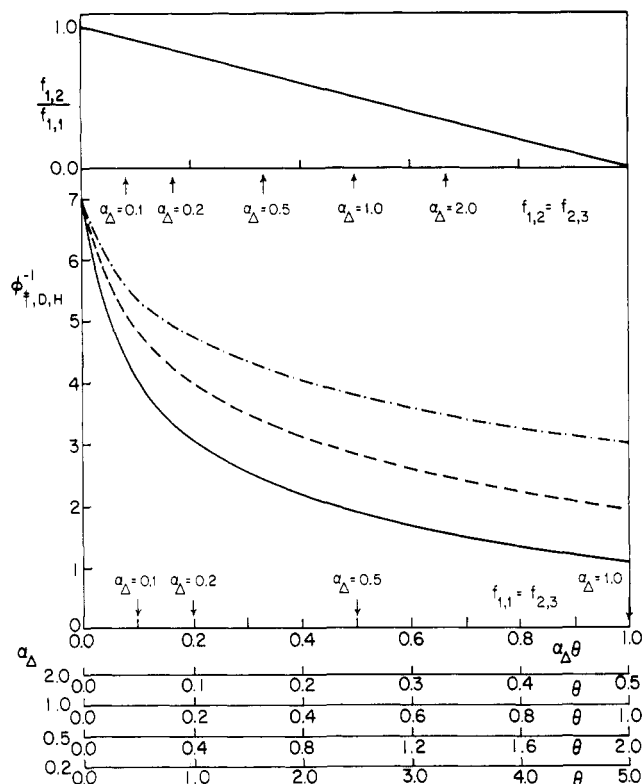


Figure 10. Variation of the observed isotope effect, $\varphi_{t,D,H}^{-1}$, as a function of θ (eq 57) for different values of α_Δ (given first) and the corresponding values of $\sum w^{1/2}$ from Figure 9 ($\alpha_\Delta, \sum w^{1/2}$): (—) 2.00, 0.59; 1.50, 0.48; 1.00, 0.38; 0.50, 0.27; 0.20, 0.20; (---) 0.50, 0.19; (—) 0.20, 0.08. The points where $f_{1,1} = f_{2,3}$ and $f_{1,2} = f_{2,3}$ are also indicated.

is close to unity because, as discussed above, the β proton is flying and the α proton is stable. In the bottom right-hand corner where the α proton is flying, the full value of 7 is found. An important result is that a significant isotope effect is found when $\alpha_\Delta\beta_\Delta > 1/4$, that is, when the heavy-atom motion is the reaction coordinate. It is common for observed isotope effects to be $\sim 2-3$, and it may be that transition states with such values do not have the proton truly in flight, but really there is a heavy-atom reaction coordinate with a reduced real hydrogenic vibration. Since, as discussed above, this region lies between the stable species and the hydrogenic transition states, one may expect to find examples of such transition states.

We can next combine the results for $\varphi_{t,D,H}$ with the complementary pattern (interchanging the α_Δ and β_Δ axes) that would be found for substitution on the β site to obtain the results displayed in Figure 11 for $(\varphi_{t,D,H}\varphi_{t,H,D})^{-1}$, which describes the effect of deuterium substitution on both sites. With these assumptions about the force constants we do not find any region where there is an abnormally large isotope effect of the order of 49. The reason for this is that the region in Figure 11 where $\varphi_{t,D,H}$ exhibits its maximum value of 7 is limited and will not overlap the corresponding region in the diagram for $\varphi_{t,H,D}$. The only way such an overlap can be achieved is to move to the left of Figure 10 at larger values of α_Δ . In terms of force constants this requires

$$f_{2,3} \ll f_{1,2} \approx f_{1,1} \quad (59)$$

The near matching of $f_{1,2}$ and $f_{1,1}$ and of their difference with $f_{2,3}$ is probably unlikely. In any case the assumption of a small value of $f_{2,3}$ decouples the two protons and reduces the system to a single proton transfer. For these reasons we consider that, although it is possible for there to be values of the force constants which could produce large isotope effects, the pattern depicted in Figure 11 is much more likely to be found in practice.

Breakdown of the Rule of the Geometric Mean

We have seen above in Figures 6 and 7 that D can be very different from zero. We now explore the effect of this on the

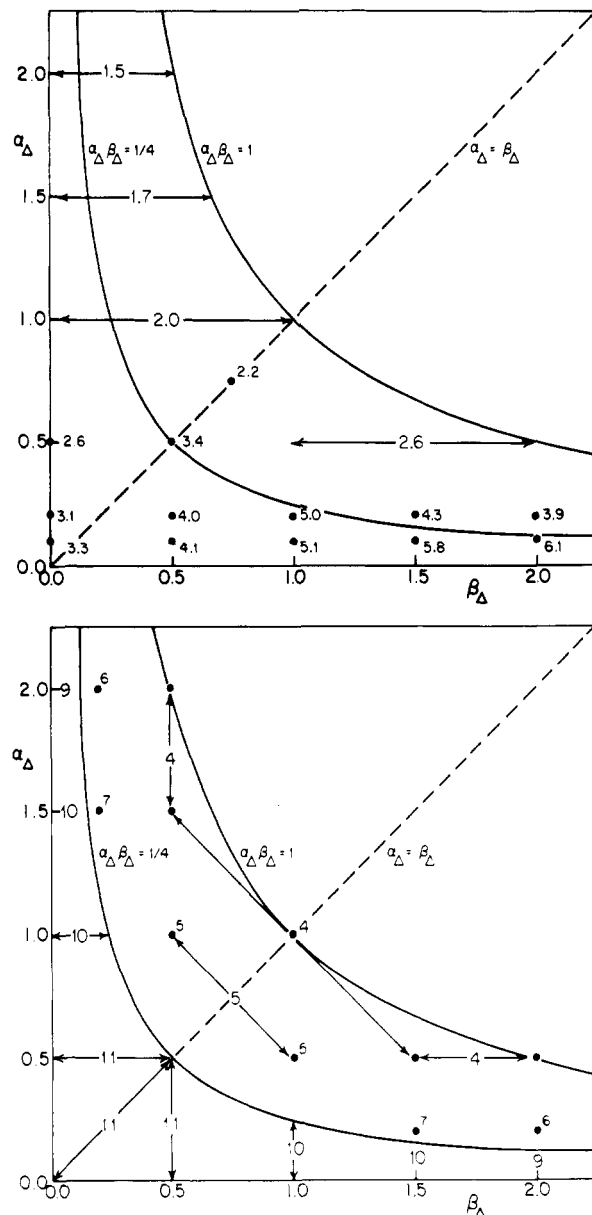


Figure 11. (Top) Variation of the observed isotope effect, $\varphi_{D,H}^{-1}$, for a single deuterium substitution with α_Δ and β_Δ assuming that $f_{1,2} \sim f_{2,3}$. (Bottom) Values for $(\varphi_{D,H}\varphi_{D,D})^{-1}$, which describes the isotope effect for double deuteration.

breakdown of the rule of the geometric mean by comparing the two fractionation factors $\varphi_{t,D,H}$ and $\varphi_{t,D,D}$

$$\varphi_{t,D,H}/\varphi_{t,D,D} = 7^{\Delta x} \quad (60)$$

where

$$\Delta x = [\theta^{1/2}/(2^{1/2} - 1)]\Delta\sum w^{1/2} \quad (61)$$

and

$$\Delta\sum w^{1/2} = \sum w^{1/2} - w_{H,D,+}^{1/2} - w_{H,D,-}^{1/2} + w_{D,D,+}^{1/2} + w_{D,D,-}^{1/2} \quad (62)$$

Values of $\Delta\sum w^{1/2}$ are displayed in Figure 12. As required by eq 58 and 62, the values are symmetrical with respect to α_Δ and β_Δ . First we notice that at large values of α_Δ and β_Δ the breakdown becomes very small. This might seem somewhat surprising since in Figure 8 D has a large positive and negative value under these conditions. The reason is that the two effects cancel, and the results in Table IV show that $\Delta\sum w^{1/2}$ tends to zero. As the negative root plunges to zero the cancellation vanishes and so the biggest deviations are found close to the $\alpha_\Delta\beta_\Delta = 1/4$ hyperbola

where

$$x' = [\theta^{1/2}/(2^{1/2} - 1)]\Delta_T \Sigma w^{1/2} \quad (65)$$

and

$$\Delta_T \Sigma w^{1/2} = \Sigma w^{1/2} - [w_{H,H,+}^{1/2} + w_{H,H,-}^{1/2} - w_{T,H,+}^{1/2} - w_{T,H,-}^{1/2}] / 1.443 \quad (66)$$

From eq 24 we find the values for w for tritium substitution are given by

$$w_{T,H} = (1/3)\{\alpha_\Delta + 3\beta_\Delta \pm [(\alpha_\Delta - 3\beta_\Delta)^2 - 3]^{1/2}\} \quad (67)$$

Values of $10^3 \Delta_T \Sigma w$, calculated from eq 28, 48, 66, and 67, are displayed in Figure 14. The pattern is similar to that found for the breakdown of the rule of the geometric mean. The largest deviation is found for the symmetrical concerted case at $(1/2, 1/2)$. Again the breakdown is of the opposite sign in the bottom left-hand corner. The reasons are the same as discussed above. The absolute value of a tritium frequency in eq 66 is lower than that of the corresponding deuterium frequency, giving a negative value of $\Delta_T \Sigma w$. The values of $\Delta_T \Sigma w$ are less than those of $\Delta \Sigma w$ displayed in Figure 12. For a value of θ of 1, we find from eq 64 to 66 that the maximum deviation is 5%. So we can conclude that the breakdown of the Swain-Schaad relation will generally be small. However, we have shown that only small breakdowns of the order of 5% will be observed when the mechanism involves two separate

single proton transfers.¹⁵ The fact that the same amount of breakdown may be observed for the concerted transition state and the two-step mechanism is a further reason why it is hopeless to use the breakdown of the Swain-Schaad relation to discriminate between the different mechanisms for double proton transfers.

Conclusions

We now summarize the main conclusions of this work.

1. In a double proton transfer reaction the reaction coordinate may be a heavy-atom vibration; the isotope effect for this case may be of the order of 2 or 3 even though both hydrogenic vibrations are real.
2. It is unlikely that isotope effects of 50 or so, corresponding to the loss of two stretching modes, will be observed.
3. For symmetrical concerted transition states there may be a substantial breakdown of the order of 15% in the rule of the geometric mean.
4. Smaller breakdowns of the order of 5% may be observed in the Swain-Schaad relation.

Acknowledgment. It is a pleasure to acknowledge helpful conversations with Prof. Knowles and Dr. Limbach. This paper was written while on leave as a Sherman Fairchild Scholar at the California Institute of Technology. I am grateful to the Institute in general and to Prof. Marcus in particular for providing such a stimulating and hospitable environment.

Registry No. Deuterium, 7782-39-0.

Kinetic Studies on the Reaction Center Protein from *Rhodospseudomonas sphaeroides*: The Temperature and Free Energy Dependence of Electron Transfer between Various Quinones in the Q_A Site and the Oxidized Bacteriochlorophyll Dimer

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(Received: February 7, 1986; In Final Form: April 16, 1986)

The temperature and free energy dependence of electron transfer from the primary semiquinone ($Q_A^{\bullet-}$) to the oxidized bacteriochlorophyll dimer $[(BChl)_2]^{+\bullet}$ have been measured in the reaction center protein from *Rhodospseudomonas sphaeroides* in which the native Q_A , ubiquinone-10, has been removed and replaced by one of 11 substituted 9,10-anthraquinones, seven 1,4-naphthoquinones, 1,2-naphthoquinone, or five 1,4-benzoquinones. For 19 of these quinones an in situ midpoint potential value at 295 K for the $Q_A/Q_A^{\bullet-}$ couple was available providing a series of reaction center proteins with a variation of reaction $-\Delta G^\circ$ from 0.49 to 0.81 eV. The $E_{1/2}$ values for the remaining Q_A s were estimated from measurements on quinones in solution, extending the reaction $-\Delta G^\circ$ range from 0.11 to 0.94 eV. The rates of intraprotein electron transfer from the various $Q_A^{\bullet-}$ molecules to $(BChl)_2^{+\bullet}$ were found to be virtually independent of temperature from 5 to 100 K and, where measured, to decrease severalfold from 100 to 300 K, a pattern well-known for native reaction center protein. Minor variations in rate at any $-\Delta G^\circ$ value are ascribable to structural differences between the quinones functioning as Q_A . A small dependence of the rate on the $-\Delta G^\circ$ was found. Preliminary attempts have been made to model the observed dependence of the electron-transfer rate on the $-\Delta G^\circ$ and temperature in terms of current theories that describe electron-transfer reactions as nonadiabatic, multiphonon, nonradiative decay processes. The results were found to be inconsistent with only one or a small number of high-frequency vibrations being coupled to electron transfer. While the addition of low-frequency modes to the analysis permits adequate explanation of the variation of rate with $-\Delta G^\circ$ at a single temperature, their use leads to the prediction that the reaction will be temperature-dependent. This is not observed. It is suggested that electron transfer from $Q_A^{\bullet-}$ to $(BChl)_2^{+\bullet}$ in reaction center protein is coupled to some distribution of high-frequency vibrations. Preliminary observations were made throughout the work on the rate of reduction of Q_A by the flash-generated reduced bacteriopheophytin ($BPh^{\bullet-}$). The rate was measured with the $-\Delta G^\circ$ of the reaction varied over an estimated range of 0.4 to 1.3 eV and at temperatures from 300 to 5 K. The temperature and free energy dependence of this subnanosecond electron transfer appears to be similar to that found for the electron transfer from $Q_A^{\bullet-}$ to $(BChl)_2^{+\bullet}$.

Introduction

Photochemical reaction center proteins are enzymes that extend across the chloroplast membrane of green plants and the intracytoplasmic membrane of photosynthetic bacteria. Pigments within these proteins absorb light energy, initiating a series of single-electron-transfer reactions, which yield a positively charged,

oxidized, high redox potential component located near one side of the membrane and a negatively charged, reduced, low redox potential component located near the other side (see ref 1-5 for

(1) (a) Okamura, M. Y.; Feher, G.; Nelson, N. In *Photosynthesis: Energy Conversion in Plants and Bacteria*; Govindjee, Ed.; Academic: New York, 1982; pp 195-272. (b) Parson, W. W.; Ke, B. *Ibid.* pp 331-385.