

Quasiclassical calculations of one-dimensional potential parameters of the hydrogen migration in *meso*-tetraphenylporphine from experimental tunnel rates

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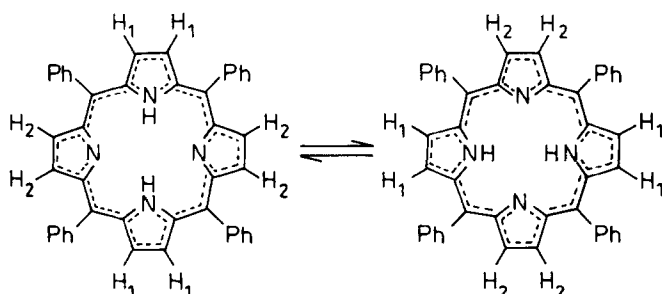
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The migration of the two inner hydrogen atoms of *meso*-tetraphenylporphine (TPP) between the four nitrogen atoms proceeds by ground state tunneling and by tunneling between the first excited degenerate NH-stretching states separated by the barrier. The experimental tunnel rates, measured previously by dynamic NMR spectroscopy, are used to compute barrier heights, E_d , and hydrogen transport distances, Δr , in quasiclassical, one-dimensional WKB approximation. Two computation methods are compared: the transmission function (TR) method and the energy splitting (ES) method. Whereas Δr is not very sensitive to the barrier type, it depends very much on the degree of cooperativity of the two-particle motion and on the computation method. There was a close agreement between the transport distances calculated from the crystallographic data of TPP and those calculated for synchronous hydrogen tunneling using the ES method. Since the TR method neglects resonance tunneling effects the transport distances calculated are too small. The calculations provide a quantitative explanation why deuterium tunneling in the two lowest ND-stretching states is too slow to be detected in the experiments. Synchronous hydrogen tunneling in TPP is then a consequence of the synchronous hydrogen motion in the potential wells.

I. INTRODUCTION

Meso-tetraphenylporphine (TPP) contains two inner hydrogen atoms that migrate between different nitrogen bonded sites as shown in scheme I:



By measuring the rate constants, $k_{\text{obs}}^{\text{H}}$ and $k_{\text{obs}}^{\text{D}}$, of the hydrogen and the deuterium migration in a wider temperature range than before with improved methods of dynamic NMR spectroscopy, we have recently shown¹ that the temperature dependence of $k_{\text{obs}}^{\text{H}}$ and $k_{\text{obs}}^{\text{D}}$ is given by:

$$k_{\text{obs}}^{\text{H}} = k_{t0}^{\text{H}} + k_{t1}^{\text{H}} \exp(-E_1^{\text{H}}/RT), \quad 160 < T < 323 \text{ K},$$

$$k_{\text{obs}}^{\text{D}} = k_{t2}^{\text{D}} \exp(-E_2^{\text{D}}/RT), \quad 213 < T < 305 \text{ K},$$

where $k_{t0}^{\text{H}} = 5.0 \pm 0.5 \text{ s}^{-1}$, $k_{t1}^{\text{H}} = \exp(26.5 \pm 1) \text{ s}^{-1}$, $E_1^{\text{H}} = 43.4 \pm 1.3 \text{ kJmol}^{-1}$, $k_{t2}^{\text{D}} = \exp(29.7 \pm 0.7)$, and $E_2^{\text{D}} = 57.3 \pm 0.3 \text{ kJmol}^{-1}$.

These results were explained with a vibrational model of hydrogen tunneling in a symmetric double minimum potential as illustrated in Fig. 1. The hydrogen migration proceeds at low temperatures at a temperature independent tunnel rate, k_{t0}^{H} , between the degenerate vibrational ground states separated by the barrier. At high temperatures, the migration proceeds mainly by tunneling from the first excited vibrational level at the tunnel

rate k_{t1}^{H} . E_1^{H} is then the energy gap between the ground state and the first excited state. Since the value of E_1^{H} was very close to the energy of the NH stretching vibration of TPP² ($\bar{\nu}_{\text{NH}} = 3315 \text{ cm}^{-1} = 40 \text{ kJmol}^{-1}$) it was concluded that the normal mode of a NH stretching vibration² becomes the reaction coordinate. The energy of activation, E_2^{D} , of the deuterium migration was found to be about twice the energy of the ND stretching vibration ($\bar{\nu}_{\text{ND}} = 2478 \text{ cm}^{-1} = 30 \text{ kJmol}^{-1}$). Therefore, the deuterium migration probably takes place between the second excited ND stretching levels.

This study deals with the calculation of barrier heights, E_d , and hydrogen transport distances, Δr , from the experimental tunnel rates in quasiclassical one-dimensional WKB approximation. Two computation methods proposed in the literature³⁻¹⁶ and three different barrier shapes are used. The transport distances calculated from the kinetic and the crystallographic data are compared and a synchronous hydrogen motion is discussed. Finally it will be shown that k_{t0}^{D} and k_{t1}^{D} are too small to be detected experimentally because of the higher mass of deuterium.

II. TUNNELING MODEL

Because of its high complexity the problem of hydrogen tunneling in TPP will be treated here in a one-dimensional quasiclassical approximation. Two methods³⁻¹⁶ have been used for computing tunnel rates in a double minimum potential. In the transmission function (TR) method the particle is regarded as oscillating in the classically allowed region with a frequency, ν_0 , attempting to tunnel through the barrier with a probability, D , which is called Gamov factor³ or transmission function. The tunneling rate, k_{tv} , from a state v is then given by

$$k_{tv} = \nu_0 D_v. \quad (1)$$

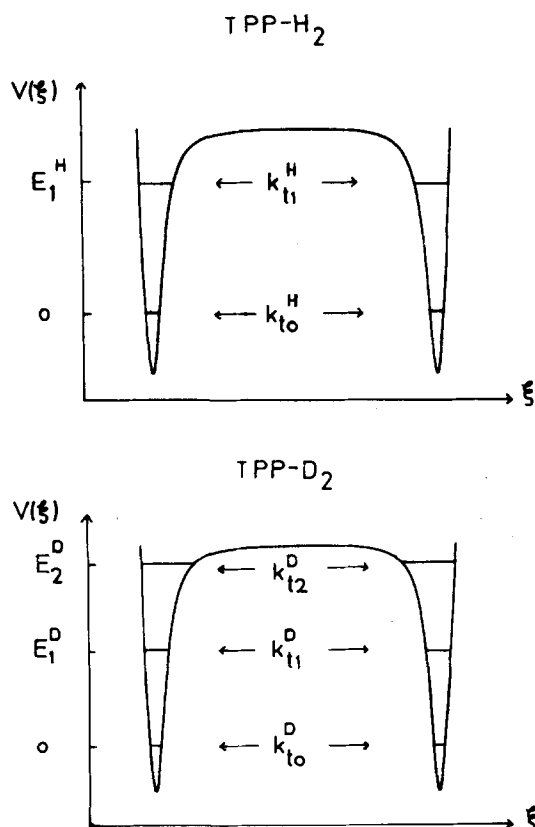


FIG. 1. Vibrational model of tunneling in TPP-H₂ and TPP-D₂. $V(\xi)$ is the potential (schematically) along the reaction coordinate. k_{tv} is the tunnel rate between the barrier separated degenerate vibrational states, v . (Reproduced with permission from Ref. 1.)

In the quasiclassical WKB approximation, D_v obeys the relation^{3,4}:

$$D_v = \exp\left(-\frac{4\pi}{h} \int_{\text{barrier region}} \sqrt{2\mu(V(\xi) - E_v)} d\xi\right), \quad (2)$$

where h is Planck's constant, $V(\xi)$ the potential along the reaction coordinate, ξ , μ the reduced mass, and E_v the energy of the moving particle.

The energy splitting (ES) method, whose origin lies in the work of Hund,⁵ relates the tunnel rates k_{tv} to the energy splittings, ΔE_v , of vibrational states caused by tunneling interaction. For a symmetrical double minimum potential, k_{tv} is given by

$$k_{tv}^{\text{ES}} = 2\Delta E_v/h. \quad (3)$$

Equation (3) follows from simple quantum mechanical arguments.^{6,7} Similar relations have been derived for asymmetrical double minimum potentials.⁷⁻¹⁰ In the quasiclassical WKB approximation the tunnel splittings, ΔE_v , are related to D_v as defined in Eq. (2), in the following way^{7,11,12}:

$$\Delta E_v = \frac{h\nu_0}{\pi} D_v^{1/2}. \quad (4)$$

Therefore, the tunnel rates are given by

$$k_{tv}^{\text{ES}} = \frac{2\nu_0}{\pi} D_v^{1/2}. \quad (5)$$

It has been pointed out by Brickmann and Zimmermann⁷⁻⁹ and others^{10,13} that, especially in the case of a symmetrical double minimum potential, the ES method predicts much higher tunneling rates than the TR method, because, in general, $D \ll 1$. This difference arises from resonance tunneling not taken into account by the TR method.

The two methods have been widely applied in explaining tunneling phenomena. The Bell treatment of tunneling in proton transfer reactions,¹⁴ for example, which assumes a continuous distribution of energy on both sides of the barrier, is based on the TR method. The TR method was equally used in problems of hydrogen diffusion in metals.¹³ The ES method was applied very early on to the calculation of tunnel splittings in intramolecular rearrangements¹⁵ such as the inversion of ammonia^{11,16} or the rotation of methyl groups.¹⁷ Since the hydrogen migration in TPP may be equally regarded as a model reaction for symmetrical proton exchange in cyclic hydrogen bonded systems^{18,19} as for intramolecular rearrangements the two methods will be applied here.

In order to compute tunnel rates, k_{tv} , from Eq. (1) or (5) a potential function, $V(\xi)$, has to be chosen. In the region of the two minima whose coordinates are $\pm\xi_0$ the quadratic potential of the harmonic oscillator is used:

$$V(\xi) = 2\pi^2\nu_0^2\mu(\xi - \xi_0)^2.$$

The barrier region is approximated by three different barrier shapes as shown in Fig. 2: (1) an inverted parabola (PB), (2) a rectangular barrier (RB), and (3) a barrier (DUB) used by Dennison and Uhlenbeck¹¹ for the ammonia inversion. The last potential is constructed from two equal parabolas connected by a straight line at the top of the barrier, E_d . The different barrier shapes are given by:

$$\text{PB: } V(\xi) = E_d(1 - (\xi/\xi_0')^2), \quad |\xi| < |\xi_0'|,$$

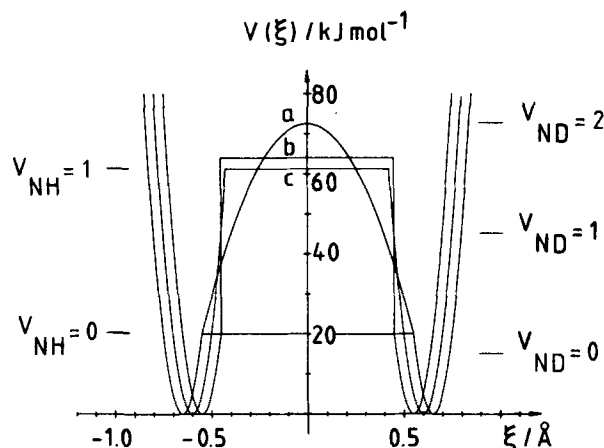


FIG. 2. Different potential functions, $V(\xi)$, of the hydrogen motion in TPP used in the calculations. (a) parabolic barrier (PB), (b) rectangular barrier (RB), (c) barrier used by Dennison and Uhlenbeck for the NH₃ problem¹⁰ (DUB). Outside the barrier region the potential is approximated by equal parabolas. The curve parameters chosen are such that the experimental values of k_{t0}^{H} and k_{t1}^{H} are reproduced using the ES model.

$$\text{RB: } V(\xi) = E_d, \quad |\xi| < |\xi'_0|,$$

$$\text{DUB: } V(\xi) = E_d, \quad |\xi| < |\xi_d|.$$

ξ'_0 is the classical turning-point in the vibrational ground state:

$$\xi'_0 = \xi_0 - \left(\frac{\hbar}{2\pi\nu_0\mu} \right)^{1/2}. \quad (6)$$

ξ_d is given by

$$\xi_d = \xi_0 - \left(\frac{E_d}{2\pi^2\nu_0^2\mu} \right)^{1/2}. \quad (7)$$

The curve parameters of Fig. 2 are chosen in a way which will allow a correlation of the experimental data as shown later.

The transmission function, D_v , for the RB and the PB are easily derived from Eq. (2):

$$D_v(\text{PB}) = \exp \left\{ -\frac{2\pi^2}{\hbar} \xi'_0 (E_d - E_v) \left(\frac{2\mu}{E_d} \right)^{1/2} \right\} \quad (8)$$

and

$$D_v(\text{RB}) = \exp \left\{ -\frac{8\pi}{\hbar} \xi'_0 [2\mu(E_d - E_v)]^{1/2} \right\}. \quad (9)$$

The transmission function for the DUB is obtained from equations of Dennison and Uhlenbeck¹¹:

$$D_v(\text{DUB}) = \left[\frac{\alpha + (\alpha^2 - 2v - 1)^{1/2}}{2v + 1} \right]^{2v+1} \times \exp \{ -(2x_0 - \alpha)(\alpha^2 - 2v - 1)^{1/2} \}, \quad (10a)$$

where

$$x_0 = \left(\frac{4\pi^2\nu_0\mu}{\hbar} \right)^{1/2} \xi_0 \quad (10b)$$

and

$$\alpha = \left(\frac{2E_d}{\hbar\nu_0} \right)^{1/2}. \quad (10c)$$

III. REACTION COORDINATE AND REDUCED MASS

Since the heavy atoms do not significantly change their position during the reaction,¹ it is a good approximation to describe the hydrogen motion by the Hamiltonian of the two-particle problem where $m_1 = m_2 = m$:

$$\mathcal{H} = -\frac{\hbar^2}{8\pi^2m} \left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} \right) + V(r_1, r_2).$$

Here r_i represents the displacement of the i th hydrogen atom from its equilibrium positions $r_i = 0$ and $r_i = \Delta r$, where Δr is the total displacement or transport distance of i .

The reaction coordinate, ξ , and the coordinate, η , which is perpendicular to ξ depend only on r_1 and r_2 but not on the reduced mass of the motion:

$$\xi = f(r_1, r_2), \quad \eta = g(r_1, r_2).$$

Examples of such relations are shown graphically in Fig. 3. The pathways 1, 2, and 4 are linear combinations of r_1 and r_2 :

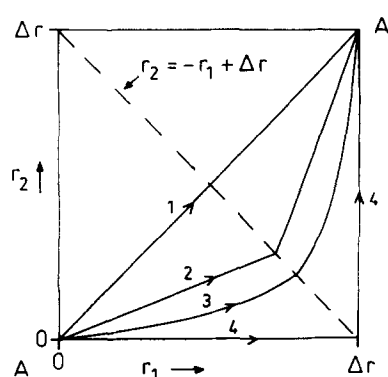


FIG. 3. Reaction coordinates, ξ , (arrows) for different pathways as a function of the displacements, r_i , of the single atoms. (1) synchronous pathway, (4) asynchronous pathway, 2 and 3: intermediate pathways. The point A characterises the system before the migration the point A' after the migration.

$$\xi = \frac{r_1 + br_2}{(1+b^2)^{1/2}}, \quad \eta = \frac{br_1 - r_2}{(1+b^2)^{1/2}}. \quad (11)$$

For the synchronous motion (pathway 1) $b = 1$, whereas for the asynchronous motion (pathway 4) $b = 0$. The total path length, $2\xi_0$, is then given by

$$2\xi_0 = 2\Delta r \frac{(1+b^2)^{1/2}}{1+b}. \quad (12)$$

Because the real pathway is not known it is convenient to adopt a definition of Schowen *et al.*²⁰ for the degree of coupling, ω , between the motion of the two atoms:

$$\omega = \left(\frac{(2-L)}{2-\sqrt{2}} \right).$$

L is the dimensionless normalized reaction path length

$$L = \frac{2\xi_0}{\Delta r},$$

which varies between $\sqrt{2}$ and 2. It follows that

$$2\xi_0 = 2 \left[1 - \omega \left(1 - \frac{1}{\sqrt{2}} \right) \right] \Delta r. \quad (13)$$

The path lengths of the synchronous ($\omega = b = 1$) and the asynchronous ($\omega = b = 0$) motion are obtained from Eq. (12) or (13):

$$2\xi_0(s) = \sqrt{2} \Delta r, \quad (14)$$

$$2\xi_0(as) = 2\Delta r. \quad (15)$$

By setting $\xi'_0 \approx \xi_0$ and by introducing Eq. (14) into Eq. (8) or (9) one can show that the synchronous hydrogen motion is equivalent to the motion of a particle with the effective mass $m_{\text{eff}} = 2m = 2m^H = m^D$ over the distance Δr . By contrast, the asynchronous motion corresponds to the motion of a particle with an effective mass $m_{\text{eff}} = m = m^H$ over the distance $2\Delta r$, thus reducing greatly the probability of tunneling.

IV. RESULTS

In order to apply Eq. (1) or (5) to the TPP system, the right term has to be multiplied²¹ by a factor of 2 because each hydrogen atom can migrate either to the nitrogen

TABLE I. Calculated barrier heights, E_d , hydrogen transport distances, Δr , for asynchronous ($\omega=0$) and synchronous ($\omega=1$) hydrogen tunneling, and deuterium tunnel rates, k_{t0}^D and k_{t1}^D . $k_{t1}^D p_{245K} = k_{t1}^D \exp(-E_1^D/RT)_{T=245K}$ is the calculated contribution to k_{obs}^D at 245 K of deuterium tunneling between the first excited ND stretching states.

Barrier type	ES method		TR method			
	PB	RB	DUB	PB	RB	DUB
$E_d/kJmol^{-1}$	73.6	64.9	61.2	74.4	65.1	62.0
$\Delta r(\omega=0)/\text{\AA}$	1.30	1.13	1.21	0.71	0.62	0.68
$\Delta r(\omega=1)/\text{\AA}$	1.84	1.60	1.71	1.00	0.88	0.96
k_{t0}^D/s^{-1}	8×10^{-7}	5×10^{-7}	4×10^{-6}	2×10^{-7}	2×10^{-7}	9×10^{-7}
k_{t1}^D/s^{-1}	1×10^4	7×10^0	4×10^2	5×10^3	6×10^0	4×10^2
$k_{t1}^D p_{245K}/s^{-1}$	5×10^{-3}	3×10^{-6}	2×10^{-4}	3×10^{-3}	3×10^{-6}	2×10^{-4}

on its right or on its left. By combining the Eqs. (1), (5), (8)–(10), and (12), one obtains k_{tv} as a function of $k_{tv} = k_{tv}(\Delta r, E_d, E_v, \nu_0, \omega, \text{barrier shape, tunneling model})$. E_d and Δr were calculated from the experimental values of k_{t0}^H and k_{t1}^H for the three barrier shapes and the two tunneling models, the cases $\omega=0$ and $\omega=1$. The frequency of the NH stretching vibration of TPP,² $\bar{\nu}_{NH} = 3315 \text{ cm}^{-1}$, was taken as classical oscillator frequency, $\bar{\nu}_0$. In order to calculate the deuterium tunnel rates, k_{t0}^D and k_{t1}^D , a value of $E_1^D = 29.7 \text{ kJmol}^{-1}$ was adopted, which corresponds to the energy of the ND stretching vibration of TPP,² $\bar{\nu}_{ND} = 2478 \text{ cm}^{-1}$. $\xi_0 - \xi'_0$ was calculated according to Eq. (6).

The results of the calculations are listed in Table I. The parameters obtained by the ES method served to construct the curves of Fig. 2. Substituting values of $\bar{\nu}_0 = 3600 \text{ cm}^{-1}$ or 3000 cm^{-1} did not significantly affect E_d and Δr . Equally, E_d and Δr do not depend very much on the value of k_{t1} . For example, for $k_{t1} = 10^{10} \text{ s}^{-1}$ and $k_{t1} = 10^{12} \text{ s}^{-1}$ one obtains by the ES method $\Delta r^{PB}(\omega=0) = 1.22$ and 1.33 \AA and $\Delta r^{RB}(\omega=0) = 1.12$ and 1.14 \AA . Equally, the factor of 2 introduced into the right term of Eq. (1) and (5) does not affect the results.

Figure 4 shows how an estimate of Δr can be obtained from the crystallographic data²² of TPP. One obtains $\Delta r = 1.66 \pm 0.08 \text{ \AA}$ for pathway a, $\Delta r = 1.84 \pm 0.08 \text{ \AA}$ for pathway b, and $\Delta r = 2.1 \pm 0.08 \text{ \AA}$ for pathway c. The value $\Delta r = 1.84 \pm 0.2 \text{ \AA}$ should, therefore, be a good estimate.

V. DISCUSSION

Whereas the barrier height, E_d , depends on the type of the barrier, the hydrogen transport distances, Δr , for the different barrier shapes, calculated from the experimental tunnel rates, do not differ very much. A similar observation has been made before¹⁶ in calculations of the height of the pyramid of NH_3 from the experimental tunnel splittings.

Table I shows that the contributions of k_{t0}^D and $k_{t1}^D p_{245K}$ to the observed rate constant of the deuterium migration,¹ which is 2.3 s^{-1} at 245 K, are negligible. This result, the consequence of the higher mass of deuterium,

applies for the whole temperature range covered in the experiments.¹

The hydrogen transport distances calculated by the TR method are too small as compared to the crystallographic data. Using the appropriate values, the TR method predicts extremely low tunnel rates, k_{t0} , of ground state tunneling, which is contrary to the experimental findings. This arises from the neglect of the resonance effect which is of special importance in symmetrical problems.

By contrast, the ES method allows a correlation of the experimental data for the case of synchronous hydrogen tunneling. There is close agreement between the distances, $\Delta r^{PB} = 1.84 \text{ \AA}$, $\Delta r^{DUB} = 1.71 \text{ \AA}$ and $\Delta r^{RB} = 1.60 \text{ \AA}$, calculated from the kinetic data, and the distance, $\Delta r = 1.84 \pm 0.2 \text{ \AA}$, calculated from the crystallographic data. It should be remembered that Dennison and Uhlenbeck,¹¹ using the quasiclassical one-dimensional approximation of Eq. (10), reproduced very well the experimental NH_3 pyramid height¹⁶ of 0.38 \AA . Although a more exact treatment should provide more exact values of E_d , those of Δr will not change appreciably. These results may, therefore, be taken as experimental evidence for the validity of the ES method in symmetrical proton exchange reactions, as predicted by Brickmann and Zimmermann.^{7-9, 15}

It can be concluded that hydrogen tunneling in TPP is a synchronous process which is facilitated by the greater transmission function, $D_v^{1/2}$, arising from the shorter barrier width, as compared to the asynchronous pathway. However, synchronous tunneling is possible only if the two particles strike the barrier at the same time. This implies a synchronous hydrogen motion even in the potential wells. Unfortunately, a normal coordinate analysis of TPP has not been made because of the complexity of the system. However, it is obvious that the two NH stretching vibrations are coupled together because of the proximity of the hydrogen atoms, and therefore, as an approximation, the system behaves like a AH_2 molecule. A normal coordinate analysis of such molecules²³ shows that the motion of the two H atoms are coupled, giving rise to a symmetric and an asym-

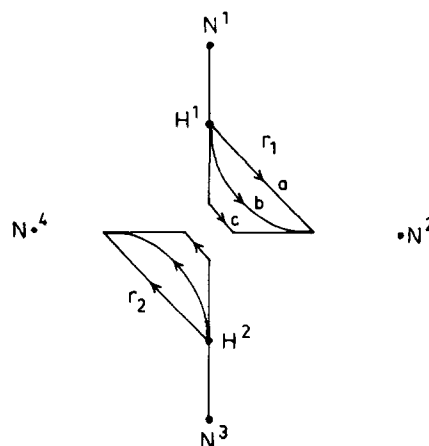


FIG. 4. Calculation of transport distances, Δr , of single hydrogen atoms from the crystallographic data.

metric stretching vibration whose normal modes are well represented by Eq. (11) with $b = 1$ if $m_A \gg m_H$. Unfortunately, the Raman-spectra of dissolved free base porphines have not been checked for the existence of a symmetric stretching vibration.²⁴

If it is so that the synchronous hydrogen motion in the potential wells enables synchronous hydrogen tunneling through the barrier, the synchronous pathway should be excluded in two-proton transfer reactions in which the two AH stretching vibrations are not coupled together. Decoupling may be realized in molecules in which the two H atoms are far away from each other or in AHD molecules where one H atom has been replaced by deuterium. Unusual primary kinetic $AH_2/AHD/ADH/AD_2$ isotope effects should result. However, the problem of measuring such effects is one for the future.

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