TUNNELING IN PROTON-TRANSFER REACTIONS IN SOLUTION

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Contents

I. Introduction

A. THE CONCEPT OF TUNNELING

In this review we are concerned with tunneling in H^+-transfer reactions. Processes in which a H^+-transfer step (eq 1) is

$$AH + B \longrightarrow A^- + HB^+ \qquad (1)$$

rate determining may usually be identified fairly unambiguously;[1,2] for instance, when the acid or base is varied, the rate constant (k) is related to the dissociation constant (K) by a relation of the Brønsted type: $k = GK^{\alpha}$, where α lies between 0 and 1. Most of the reactions to be considered are undoubtedly of this type. Since the groups A and B are commonly much heavier than the proton, it is a good approximation to suppose that the proton moves between two centers which remain at a fixed distance.[3] The reaction can therefore be represented on a potential-energy diagram (Figure 1) in which the abscissa represents the distance x of the proton from one of the centers.

The concept of tunneling has become familiar in various fields, such as radioactive decay, electron emission from metals, and electron-transfer reactions; it now finds a place in textbook expositions of wave mechanics. Whereas classical theory predicts that a particle can cross a potential-energy barrier only if its energy is greater than the barrier height, quantum theory predicts that particles with less energy may also pass from one side of the barrier to the other. This may be seen in a qualitative way from the uncertainty principle, as follows.

Consider a particle incident upon a one-dimensional energy barrier. On the classical picture (Figure 2a), the position (x) and energy of the particle may be represented by a point P. If the energy W of the particle is less than the height E of the barrier, it cannot escape, while if $W > E$ it will always escape; thus the probability of escape rises abruptly from zero to unity at $W = E$, as in Figure 2b. The particle can be pictured as a ball rolling up the energy profile, and metaphorically we speak of it as "passing over" the barrier.

In the quantum-mechanical account, however, it is no longer possible to specify exactly both the energy (W) and the position (x) of a particle. If the energy is specified as W as before ($W < E$), the position becomes indeterminate, and there is a finite probability that the particle will be detected on the far side of the barrier. Since such a particle cannot be supposed to pass "over" the barrier, it may be said (again metaphorically) to "pentrate" or "tunnel through" the barrier. But these expressions must not be taken literally. The region "inside" the barrier corresponds to a total energy of the particle less than its potential energy, so that if we were to insist on using particle language the kinetic energy would be negative and the velocity would therefore be imaginary. It is evident that we cannot visualize the particle as it "goes through" the barrier, and attempts to do so will lead to confusion. The problem is better approached in terms of the wave picture of matter, as follows.

It is well known that to account for certain phenomena, whether of matter or of radiation, we must use a particle model, while for others (such as diffraction) we must use a wave model. In some situations the system must be considered on the analogy of a particle, in others on the analogy of a wave. A system of mass m and velocity v is associated with a

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(1) R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, 1941, Chapters 7 and 8.

(2) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapters 9 and 10.

(3) Estermann and O. Stern, *Z. Physik.*, 53, 779 (1929).

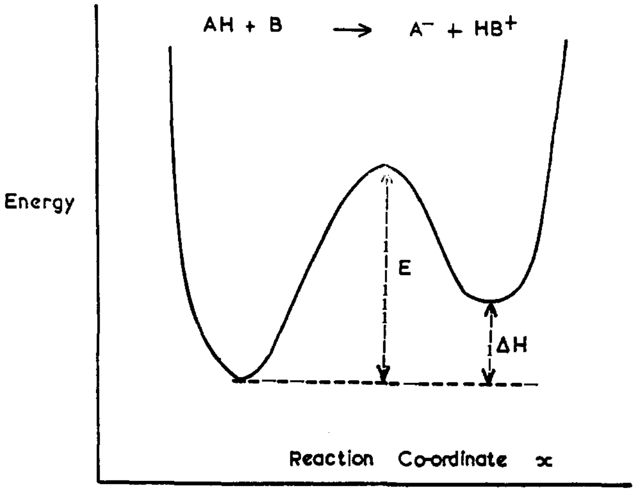

Figure 1. Potential-energy diagram for a proton-transfer reaction.

wavelength λ given by the de Broglie relation $\lambda = h/mv$. The wave properties of a system become important only if the wavelength is large enough in relation to the process concerned, so that although all systems have these properties they will be most easily detected when the mass is small. Electrons, for instance, exhibit diffraction at a crystal lattice, and similar effects have been observed for hydrogen and helium atoms.[3,4] Protons in thermal equilibrium at ordinary temperatures are associated with a wavelength between 1 and 2 Å, if we assume that they have kinetic energy in two degrees of freedom.

$$\lambda = h/mv = h/(2m[KE])^{1/2} = h/(2m\mathbf{k}T)^{1/2} = 30.8/T^{1/2} \quad (2)$$

These wavelengths (in Å) are comparable with the width expected for the energy barrier in a proton-transfer reaction, which may be roughly estimated by comparing the least distance of approach in a nonreactive collision, as given by the van der Waals radii of the atoms concerned, with the length of the bond formed. Such reactions must therefore be treated quantum mechanically. To do this, we represent the proton by the Schroedinger wave equation, and the proton transfer by the incidence of such a wave on the energy barrier, as in Figure 3a, which shows the variation of ψ with distance superimposed on a particular barrier. The wave equation involves the potential energy of the proton, and to represent the proton-transfer process we substitute into it the expression for the potential-energy barrier. The resulting equation can be solved in simple cases (see below). For proton energies lower than the barrier height, the solutions show that besides the reflected wave, which would be expected if the proton had no chance of crossing the barrier, there is also a transmitted wave; that is, there is a finite probability that the proton will "penetrate" the barrier. The reaction probability rises with the energy of the proton, as shown in Figure 3b, which may be compared with Figure 2b. The steepness of the curve depends on the slope and especially on the thickness of the barrier.

That this behavior is to be expected for a wave, though not for a particle, may be seen from an optical analogy.[1] Consider a light-ray traveling in a block of glass (Figure 4a) and meeting a glass-to-air interface at an angle such that total internal reflection occurs. This interface corresponds to a potential wall, and on a particle theory of light the less dense medium should be quite unaffected. According to the wave theory, however, it experiences a disturbance, though this falls off sharply and becomes negligible at a distance of a few wavelengths. If another block of glass is brought up within a short distance *d* of the first (Figure 4b), an appreciable fraction of the light energy appears in a ray transmitted across the gap, which corresponds to a potential-energy barrier. The intensity of the transmitted ray decreases exponentially with increase of the distance *d*. The effect is easily demonstrated with microwaves, using blocks of paraffin wax as the denser medium.

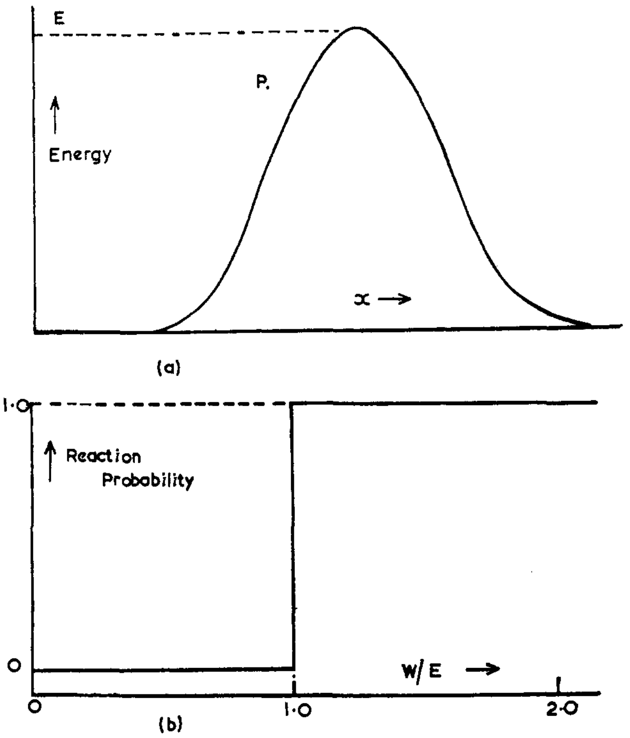

Figure 2. Incidence of a proton on a potential-energy barrier of height *E* (classical version): (a) potential energy *V*(*x*) against reaction coordinate *x*; (b) reaction probability against energy *W* of proton expressed as *W*/*E*.

It is to be noted that tunneling is a necessary consequence of the use of the wave model, which is fundamental to the view of matter on which quantum mechanics is based. The question is not whether tunneling occurs, but whether it is detectable. If the basic principles of quantum mechanics are accepted, it follows that the behavior of atoms cannot be treated in terms of the particle model alone. For most atoms and groups, the effects of tunneling are negligible, but for light atoms they may not be, and detailed consideration of the wave model is needed. The theory of tunneling is simply the application of the wave model. Where this model is appropriate, the use of the particle model may lead to a misleading picture of the situation. We must not imagine, for instance, that some protons go "over" the barrier and some "through" it; since the particle model is fundamentally inappropriate, we cannot use it in this way. It is not even true that all protons with energy greater than the barrier height will cross the barrier; curves such as those in Figure 3b show that *G* is less than unity even for these, indicating that partial "reflection" occurs.

The kinetic consequences of this view of reactions must

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(4) T. H. Johnson, *Phys. Rev.*, 37, 847 (1931).

now be considered and compared with experiment. We confine our attention to the evidence from the rates of homogeneous chemical reactions involving the transfer of H or of its isotopic modifications D and T. The evidence from spectroscopy and from electrochemical phenomena, though of great interest, will not be discussed in this review.

B. LIST OF SYMBOLS

W		total energy
$V(x)$		potential energy corresponding to reaction coordinate x
E		height of energy barrier
E^{H}, E^{D}, E^{T}		height of energy barrier for transfer of H, D, T
E_{A}, E_{obsd}		empirical Arrhenius activation energy given by $\mathrm{d}\ln k/\mathrm{d}(1/T)$
$2a$		width of parabolic barrier
α	=	$E/\mathbf{k}T$
β	=	$2\pi^2 a(2mE)^{1/2}/h$
γ	=	$1 - W/E$
c_t	=	$2E/a^2$
ν_t	=	$(2\pi\mathbf{k}T/h)(\alpha/\beta) = E^{1/2}/\pi a(2m)^{1/2} = c_t^{1/2}/2\pi m^{1/2}$
u	=	$2\pi\alpha/\beta = h\nu_t/\mathbf{k}T$

C. THE KINETIC CONSEQUENCES OF TUNNELING

The kinetic consequences of tunneling in proton-transfer reactions may be calculated as follows. The fraction of protons of a given energy that pass the barrier, which may be called the "reaction probability" or the "permeability" of the barrier for protons of that energy, is the ratio of the squares of the amplitudes of the transmitted and incident waves; this is found from the solution of the wave equation. The observed rate of reaction involves a large number of systems with different energies, so the reaction probability must be suitably averaged; this may be done by assuming a Boltzmann distribution of energies, which is true for any system in thermal equilibrium. One can then calculate the rate of reaction for a given barrier. Solutions of varying exactness have been derived for barriers of various shapes (see below). It emerges that, regardless of the shape of the barrier, the following general behavior can be expected.[1,2]

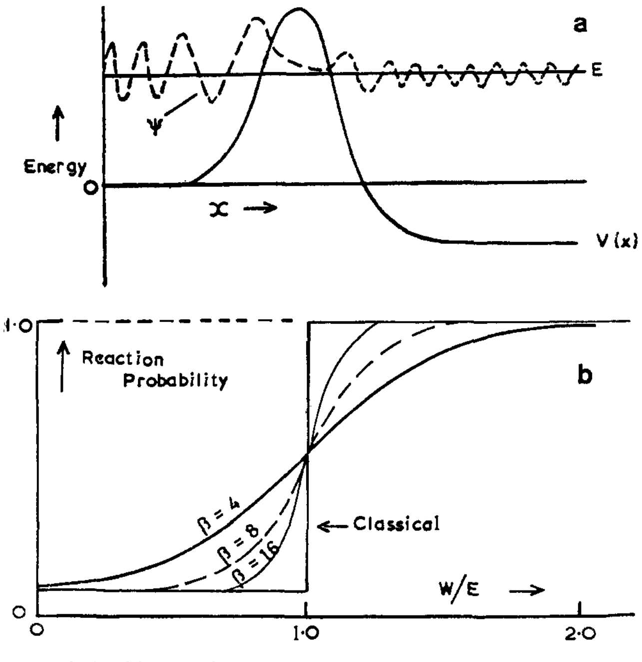

Figure 3. Incidence of a proton on a potential-energy barrier of height E (quantum-mechanical version): (a) variation of ψ with x, superimposed on potential-energy diagram $V(x)$ against x (after D. L. Bunker); (b) reaction probability against energy W of proton, expressed as W/E, for various parabolic barriers (after Johnston and Rapp[10]). The parameter β is related to the barrier dimensions.

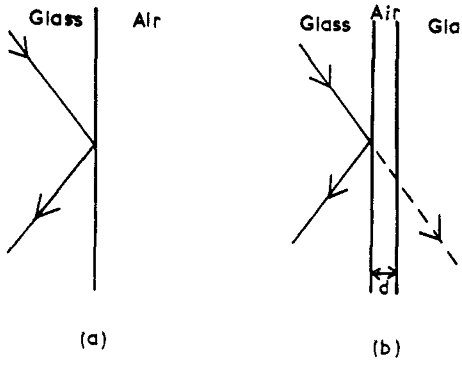

Figure 4. Optical analog of tunneling.

1. Nonlinear Arrhenius Plots

For most reactions the variation of the rate constant k with temperature is given by the empirical Arrhenius equation $k = A\exp(-E_{\mathrm{A}}/RT)$ within experimental error. The equation may be written in the form

$$\ln k = \ln A - E_{\mathrm{A}}/RT \tag{3}$$

whence

$$\mathrm{d}\ln k/\mathrm{d}(1/T) = -E_{\mathrm{A}}/R$$

A plot of $\ln k$ against $1/T$ is therefore linear, and its slope is constant and equal to $-E_{\mathrm{A}}/R$. The A factor is evidently given by $(\ln k + E_{\mathrm{A}}/RT)$.

The Arrhenius equation approximates closely to the equations predicted on the simplest assumptions by the collision and transition-state theories for reactions in which a system must surmount an energy barrier, so that the reaction probability jumps from 0 to 1 at a particular energy (Figure 2b). The temperature dependence of the rates calculated for tunneling does not follow this law, especially at low temperatures. Some typical values of the rate constants for proton and deuteron transfer, calculated for a parabolic barrier, are shown in Figure 5 in the form of Arrhenius plots. The linear plot calculated from the expression in which tunneling is ignored, $k = A\exp(-E/RT)$, is shown for comparison. For proton transfers, it is evident that as the temperature falls (from left to right) the rate constant falls off less steeply than it would in the absence of tunneling; the plot is not linear but concave upward. The physical reason for this increasing positive deviation with decrease of temperature is that, although the fraction of systems with energy less than the barrier height decreases, according to the Boltzmann law, such systems have still a finite chance of passing the barrier. The deviation from linearity is markedly dependent on the width of the energy barrier; compare the curves in Figure 5 for barrier widths of

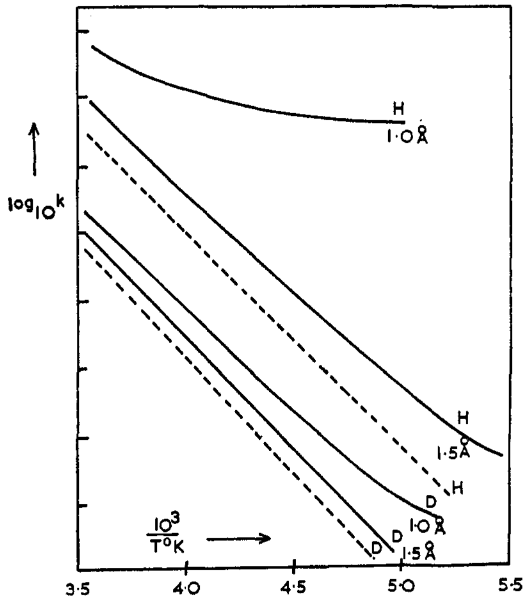

Figure 5. Arrhenius plots of log k against $1/T$ for proton- and deuteron-transfer reactions: (a) calculated from the Arrhenius equation without tunneling (dashed lines), and (b) calculated for tunneling through a parabolic barrier (full lines). The height of the barrier for proton transfer E^H is 15 kcal mole^{-1}, and for deuteron transfer E^D is 16 kcal mole^{-1}. The width is shown beside each line. Heat of reaction $\Delta H = 1$ kcal mole^{-1}.

1.5 and 1.0 Å. There should, then, be a temperature range in which deviations from a linear Arrhenius plot can be observed; but this range is difficult to predict, since we have no accurate knowledge of the dimensions of energy barriers.

The slope of the linear Arrhenius plot in the absence of tunneling gives E, the height of the energy barrier. The barrier heights will be designated as E^H for the proton transfer, E^D for deuteron transfer, and E^T for triton transfer. For the nonlinear plots calculated for tunneling, the gradient of the curve at any temperature gives the apparent energy of activation that would be derived from rate measurements made close to that temperature (*cf.* eq 3). It is evident that these observed values, which we will write as E^H_{obsd}, E^D_{obsd}, and E^T_{obsd}, will decrease as the temperature falls, especially E^H_{obsd}. They will be less than the barrier heights, the difference being largest for $E^H - E^H_{obsd}$. Plots of E^H_{obsd} and E^D_{obsd} against temperature, derived from plots in Figure 5, are shown in Figure 6.

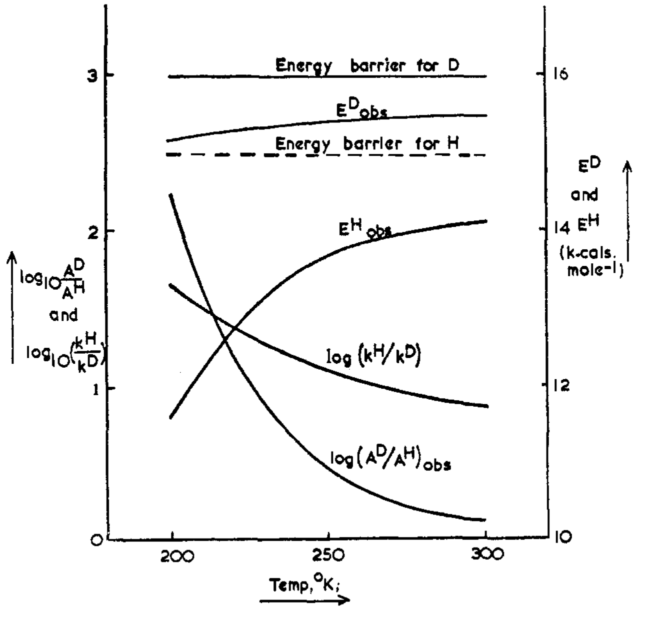

Figure 6. Plots derived from Figure 5, showing the variation with temperature of E^H_{obsd}, E^D_{obsd}, k^H/k^D, and A^D_{obsd}/A^H_{obsd}. The heights of the energy barriers, as in Figure 5, are (in kcal mole^{-1}) $E^H = 15$, $E^D = 16$, $\Delta H = 1$. The width of the parabolic barrier is $2a = 1.5$ Å.

2. *Anomalous Isotope Effects*

The deviations calculated for the transfer of D^+ or T^+ are much smaller than for H^+, because the associated de Broglie wavelengths are shorter than those of the proton. Figure 5 illustrates this point; the curves for deuteron transfer are much closer to the line calculated without taking tunneling into account than are those for proton transfer. Several consequences follow.

(i) The rate ratio k^H/k^D is larger than it would be in the absence of tunneling, and the deviation increases with decrease of temperature. This can be seen from the vertical distance between the curves for H^+ and D^+ transfer in Figure 5 and is shown in Figure 6. The maximum value of k_H/k_D that can be explained without tunneling is calculated by supposing that all the zero-point energy associated with the A–H or A–D bond is lost in the transition state, so that the activation energy for the deuteron transfer is higher by the difference of the zero-point energies of these bonds; the value so obtained[5,6] is around 7 at 25°, if stretching alone is taken into account. (If the zero-point energy for bending also is assumed to be lost, which is less likely, the value is 17.) Larger values are anomalous and suggest that tunneling should be taken into account. Much smaller values may also be significant if they deviate from an otherwise regular relation between k^H/k^D and the equilibrium constant of the reaction (see below).

(ii) The difference in the observed activation energies for the two isotopes ($E^D_{obsd} - E^H_{obsd}$) is larger than it would be in the absence of tunneling ($E^D - E^H$). This can be seen from Figure 5, which shows that at any temperature E^H_{obsd} deviates from E^H more than E^D_{obsd} does from E^D; the corresponding values are plotted in Figure 6. The maximum value of ($E^D - E^H$) corresponds to the difference of zero-point energy for the stretching of the C–D and C–H bonds, which is usually in the region of 1.1 kcal mole^{-1}. Any value of ($E^D_{obsd} - E^H_{obsd}$) larger than this suggests that tunneling may have to be taken into account.

(iii) The apparent A factor for proton transfer (A^H_{obsd}) is greater than that for deuteron transfer (A^D_{obsd}). This may be seen by extending the Arrhenius plots as in Figure 7, which is similar to Figure 5 but extends to $1/T = 0$ on the left. From eq 3 it is evident that the intercept on the Arrhenius plot when $1/T = 0$ is ln A_{obsd}. Suppose that the rate constants k^H and k^D are measured over the temperature range 250–220°K, and that this is not long enough for the nonlinearity

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(5) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949); *Pure Appl. Chem.*, **8**, 217 (1964).

(6) J. Bigeleisen in "Tritium in the Physical and Biological Sciences," Vol. I, IAEA, Vienna, 1962, p 161.

of the plot to be detectable. The values of A^{H}_{obsd} and A^{D}_{obsd} that would be derived from such results may be seen by extrapolation to $1/T = 0$, as in Figure 7. It is seen that $A^{D}_{obsd} > A^{H}_{obsd}$. This is quite anomalous from the point of view of collision theory, in which A depends on the collision number and on steric factors, so that it cannot be appreciably larger for deuteron than for proton transfer; since the isotopic molecules AH and AD differ little in mass or shape, we should expect that $A^{D}_{obsd}/A^{H}_{obsd} \simeq 1$. Transition-state theory likewise predicts that $A^{D}_{obsd}/A^{H}_{obsd}$ will not usually be greater than unity; the maximum value is 2, and this supposes an improbable state of affairs in the transition state.[5] Any larger value of $A^{D}_{obsd}/A^{H}_{obsd}$ is anomalous and suggests that tunneling should be taken into account. Similar considerations apply to $A^{T}_{obsd}/A^{H}_{obsd}$. Such an indication of tunneling is particularly striking because there is no obvious alternative explanation.

If values of $A^{D}_{obsd}/A^{H}_{obsd}$ were determined over a temperature range in which a change in E^{H}_{obsd} was detectable, we should expect a change in the values with temperature, as shown in Figure 6. This case has not yet been realized experimentally; changes in E^{H}_{obsd} have been reported only at temperatures where the deuteron-transfer reaction has become too slow to follow.

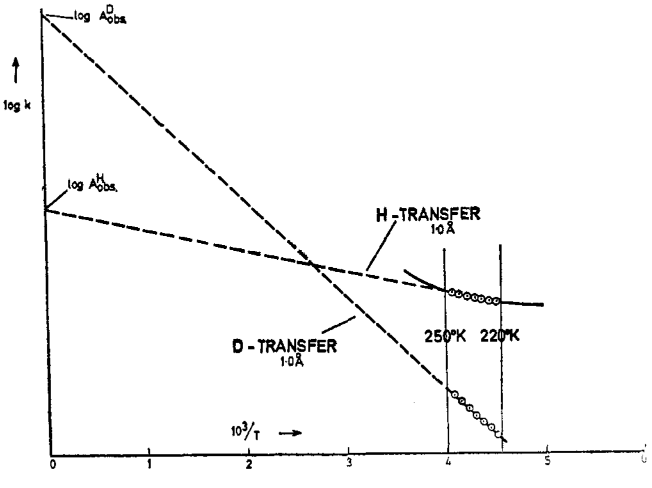

Figure 7. Extrapolation to $1/T = 0$ from Arrhenius plots for tunneling through a parabolic barrier. The barrier heights are as in Figure 5; the width is taken as 1.0 Å.

(iv) Comparison of the rate constants for proton, deuteron, and triton transfer (k^{H}, k^{D}, and k^{T}) at a single temperature may show an anomaly. In the absence of tunneling, the relation between k^{H}/k^{D} and $k^{H}k^{T}$ is given, on the simplest assumptions, by Swain's equation[7]

$$\log (k^{H}/k^{T}) = r \log (k^{H}/k^{D}) \quad (4)$$

where $r = 1.442$. The derivation has been generalized by Bigeleisen,[6] who has shown that the factor r may be as high as 1.58 if the isotope effect is temperature independent, or as low as 1.33 for small isotope effects at very high temperature, but that normally it should be close to Swain's value of 1.442. Lewis has pointed out[8] that tunneling may lead to deviations from this value, although it will not necessarily do so.

3. The Interest of the Results–Barrier Dimensions

Besides its obvious interest as a possible explanation of anomalous isotope effects and nonlinear Arrhenius plots, quantum-mechanical tunneling is of interest because its effects depend very markedly on the width of the potential-energy barrier. Rate measurements that can be confidently interpreted in terms of tunneling are therefore a means of investigating the dimensions of energy barriers, on which there is remarkably little other information. The dimensions derived from the experimental results depend, as we shall see, on the shape assumed for the barrier, and their absolute values therefore cannot be relied upon; but their relative values in a series of related reactions, or a series of solvents, should be of interest.

II. Sketch of the Mathematical Theory of Tunneling in Chemical Reactions

A. THE ECKART BARRIER

We first assume that there is a unique potential-energy profile for the movement of the proton along the reaction coordinate, as in Figure 1. This is equivalent to assuming that, on the potential-energy surface, the only path that need be considered is the path of minimum potential energy, along the bottom of the valley and over the lowest point of the saddle. (This restriction can later be removed.)

1. Solution of the Wave Equation

The Schroedinger equation representing wave motion in one dimension along the reaction coordinate x may be written

$$(\mathrm{d}^2\psi/\mathrm{d}x^2) + (8\pi^2\mu/h^2)[W - V(x)]\psi = 0 \quad (5)$$

Here W is the total energy of the wave particle, $V(x)$ is its potential energy at x, and μ is the reduced mass, which in our problem can be identified with the mass of the proton. To represent the incidence of a proton on a potential-energy barrier, we must insert for $V(x)$ the function representing the form of the barrier and solve the resulting equation. It is evident that when $W - V(x)$ is effectively constant, at a considerable distance on either side of the barrier, the equation becomes

$$(\mathrm{d}^2\psi/\mathrm{d}x^2) + (\text{constant})\psi = 0 \quad (6)$$

This is the equation for a sinusoidal wave, as shown in Figure 3a. We wish to calculate the ratio of the amplitudes of the waves on the left and right, since the square of this ratio gives the permeability of the barrier.

A type of barrier for which an exact solution can be obtained is the Eckart barrier,[9-12] of which a symmetrical form

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[7] C. G. Swain, E. C. Stivers, J. F. Reuwer, and L. J. Schaad, *J. Amer. Chem. Soc.*, 80, 5885 (1958).

[8] E. S. Lewis and J. K. Robinson, *ibid.*, 90, 4337 (1968).

[9] C. Eckart, *Phys. Rev.*, 35, 1303 (1930).

[10] H. S. Johnston and D. Rapp, *J. Amer. Chem. Soc.*, 83, 1 (1961).

[11] H. S. Johnston, *Advan. Chem. Phys.*, 3, 131 (1960).

[12] T. E. Sharp and H. S. Johnston, *J. Chem. Phys.*, 37, 1541 (1962).

is shown in Figure 8 and an unsymmetrical form in Figure 3. The potential energy for this barrier is defined by

$$V(x) = [A\exp(2\pi x/l)]/[1 + \exp(2\pi x/l)] + [B\exp(2\pi x/l)]/[1 + \exp(2\pi x/l)]^2 \quad (7)$$

where A, B, and l are constants. This function $\longrightarrow 0$ for large negative values of x, and A for large positive values; thus for the symmetrical barrier (Figure 8) $A = 0$, while for the unsymmetrical barrier A represents the heat of reaction (Figure 3). The effective width of the transition region is of the order of $2l$.

When the equation defining this barrier (eq 7) is combined with the Schroedinger eq 5, one obtains an equation of the hypergeometric type, whose solution may be written down in terms of the hypergeometric series. For large positive values of x, corresponding to completion of the proton transfer, this solution reduces to an equation representing a single transmitted wave

$$\psi = a\exp(2\pi ix/\lambda') \quad (8)$$

where

$$\lambda' = h/(2m[W - A])^{1/2}$$

For large negative values of x, the solution represents two waves, one incident and one reflected, corresponding to the protons approaching the barrier and those not transmitted

$$\psi = a_1\exp(2\pi ix/\lambda) + a_2\exp(-2\pi ix/\lambda) \quad (9)$$

where $\lambda = h/(2mW)^{1/2}$. The quantity $\rho = (a_2/a_1)^2$ may be called the reflection coefficient; the transmission coefficient or permeability G of the barrier is $(1 - \rho)$. These may be expressed in terms of the barrier parameters A, B, and l and the energy W of the incident particle. The equation is

$$\rho = |a_2/a_1|^2 = \left|\frac{\Gamma[\frac{1}{2} + i(\delta - \beta - \alpha)]\Gamma[\frac{1}{2} + i(-\delta - \beta - \alpha)]}{\Gamma[\frac{1}{2} + i(\delta - \beta + \alpha)]\Gamma[\frac{1}{2} + i(-\delta - \beta + \alpha)]}\right|^2 \quad (10)$$

where $\alpha = 1/\lambda$, $\beta = 1/\lambda'$, $C = h^2/8ml^2$, $\delta = {}^1/_2[(B - C)/C]^{1/2}$. If the barrier is not too narrow, $B > C$ and eq 10 gives for the permeability G of the barrier to protons of energy W.

$$G(W) = 1 - \rho = \frac{\cosh[2\pi(\alpha + \beta)] - \cosh[2\pi(\alpha - \beta)]}{\cosh[2\pi(\alpha + \beta)] + \cosh[2\pi\delta]} \quad (11)$$

The form of this variation of G with W is similar to that illustrated in Figure 3b.

2. *Derivation of the Kinetic Equation*

The next step is to combine this expression for the permeability of the barrier to protons of a given energy, which is the same as the reaction probability for protons of that energy, with the fraction of the protons possessing that energy. The system will be assumed to be in thermal equilibrium, so the Boltzmann distribution will hold. The simplest form of the equation for the fraction of protons with energies between W and $W + dW$ is

$$\frac{dN}{N} = \frac{1}{kT}\exp(-W/kT)\,dW \quad (12)$$

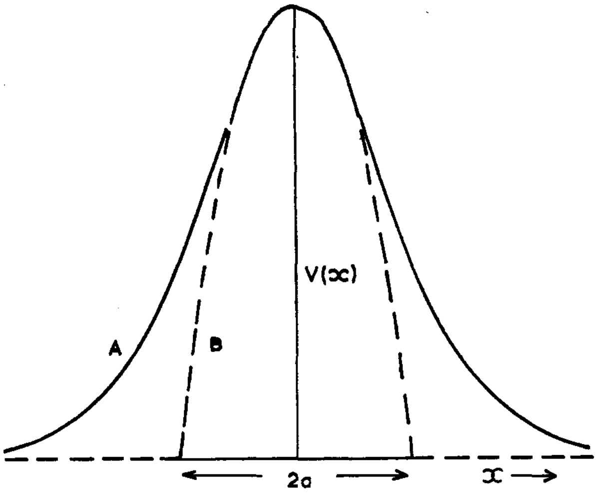

Figure 8. Symmetrical Eckart barrier (A) and parabolic barrier (B). The curvature at the top of each barrier is the same.

This is strictly true only when the energy is expressible as two square terms and is nonquantized. It is thus valid for translational kinetic energy of the reacting molecules along the line of centers. When applied to vibrational or rotational energy, it implies a neglect of quantization, and in particular of the zero-point energy, but will be a reasonable approximation if the temperature is not too low.

To obtain a quantity proportional to the rate of reaction, we multiply this expression by the reaction probability, $G(W)$, corresponding to the energy W, and integrate over all possible values of W. The product is

$$v = \int_0^\infty (1/kT)G(W)\exp(-W/kT)\,dW \quad (13)$$

If we had ignored tunneling, we should have put $G = 0$ when $W < E$, and $G = 1$ when $W > E$, and so should have obtained an expression for classical behavior.

$$v_{\text{class}} = \int_E^\infty (1/kT)\exp(-W/kT)\,dW = \exp(-E/kT) \quad (14)$$

The ratio Q of the two expressions for the rate is

$$Q = v/v_{\text{class}} = \exp(E/kT)\int_0^\infty (1/kT)G(W) \times \exp(-W/kT)\,dW \quad (15)$$

This is the tunneling correction factor which would have to be applied to any value of the rate constant that had been calculated without taking account of tunneling. For instance, on simple collision theory such a value is $k = PZ\exp(-E/kT)$, where Z is the collision number and the factor P corrects for steric and other effects. The corresponding expression for k that takes account of tunneling is thus

$$k = PZ\int_0^\infty (1/kT)G(W)\exp(-W/kT)\,dW \quad (16)$$

When we insert in eq 15 or 16 the expression for $G(W)$ given in eq 11, the result is not susceptible of exact integration. Numerical integrations have been carried out[10-13] and con-

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(13) E. M. Mortensen and K. S. Pitzer in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 57.

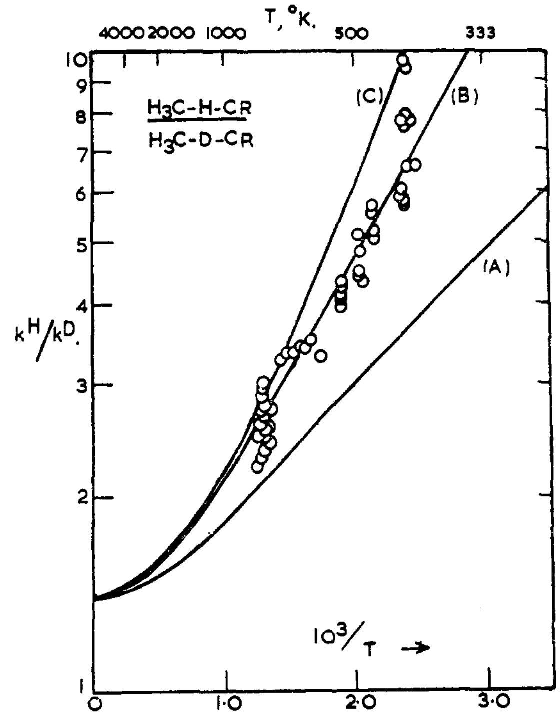

Figure 9. Calculated and observed kinetic isotope effect for reactions of methyl radicals with ethane and acetone: circles, experimental points; curves, calculated. A, no tunneling; B, tunneling, Eckart potential, not restricted to single path; C, tunneling, one-dimensional Eckart barrier. Reproduced by permission from *J. Amer. Chem. Soc.*, **83**, 1 (1961).

venient tables have been published.[14a] An approximate expression which gives good results in chemically interesting cases has also been obtained by Shin.[14b] A simplified form, applicable when $E \simeq \Delta H$ and ΔH is considerable, has been given by Weiss.[14c] The lack of an exact and general analytical solution is nonetheless a disadvantage.

In summary, then, the Eckart barrier gives an exact solution to the wave equation and an exact expression for the permeability of a barrier of given energy, but the form of this expression is not in general convenient for the second stage of the calculation, when the permeability has to be combined with the Boltzman distribution to give a rate constant.

3. *Extension to More Than One Reaction Path*

Thus far we have assumed that there is a unique reaction path, so that a treatment in terms of a single reaction coordinate x is adequate. This is not strictly true; there are alternative paths on the potential-energy surface (corresponding to different configurations of the activated complex) along which tunneling might also occur. (The mathematical condition for these paths to be important is that the de Broglie wavelength for the atom transferred is large compared to the parabolic region near the top of the barrier.)

The treatment has been extended to include such paths by Johnston and Rapp[10,11] who fitted Eckart potentials to sections through the potential-energy surface parallel to the reaction coordinate and carried out the multiple integration numerically by computer. They applied this method to the reaction $H + H_2 \rightarrow H_2 + H$ and found that, assuming the two-dimensional treatment to be correct, the one-dimensional Eckart barrier overestimates the tunneling correction by a factor of 3 at 333°K and 1.4 at 500°K (see also Figure 9). These conclusions conflict, however, with some results by Mortensen and Pitzer,[18] who solved the two-dimensional Schroedinger equation numerically, and found that the one-dimensional Eckart barrier underestimated the correction by a factor of the order of 0.6. Further calculations must be awaited before a conclusion can be reached about the quantitative reliability of calculations from the one-dimensional equation; some further evidence is mentioned in section III. There is no doubt, however, about the general form of the results as outlined in section I.

B. THE PARABOLIC BARRIER

1. *Bell's Earlier Treatment*

A type of barrier that is more convenient for kinetic calculations is the parabolic barrier. We consider first a symmetrical truncated parabola, as represented in Figure 8; this corresponds to a reaction with zero heat of reaction. The equation for the potential energy, if the width of the parabola at the base is $2a$ and the height is E, is

$$V(x) = E[1 - (x^2/a^2)] \tag{17}$$

This type of barrier was originally treated by Bell,[1,15] who noted that the discontinuity of shape at the base of the parabola might lead to inaccurate results for very small values of W. He used an approximate solution of the Schroedinger equation (the Brillouin–Wenzel–Kramers approximation[16]), which is valid when W is considerably less than E, but becomes less accurate as W approaches E. He also assumed that $G = 1$ when $W \geqslant E$, whereas the accurate solution for the Eckart barrier shows that $G < 1$; this approximation will lead to inaccuracy for small positive values of $(W - E)$, an energy range which will be important when the degree of tunneling is small. The result when $W < E$ is

$$G = \exp\{-\beta[1 - (W/E)]\} \tag{18}$$

where

$$\beta = 2\pi^2 a(2mE)^{1/2}/h$$

The accuracy of this approximate solutions was tested in two ways. (a) An exact solution was obtained[17] for the special case $W = E$, and it was found that $G \simeq 1/2$, so that the approximate treatment is here in error by a factor of 2; this is the maximum error that will arise. (b) A comparison with the values of G derived from the Eckart barrier for a range of values of W showed a maximum difference of the same order.[15] It was concluded that the equations could be used for semiquantitative calculations and should be fairly accurate for the relative rates of similar reactions.

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[14] (a) H. S. Johnston and J. Heicklen, *J. Phys. Chem.*, **66**, 532 (1962); (b) H. Shin, *J. Chem. Phys.*, **39**, 2934 (1963); (c) J. J. Weiss, *ibid.*, **41**, 1120 (1964).

[15] R. P. Bell, *Proc. Roy. Soc.*, **A148**, 241 (1935).

[16] L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p 198.

[17] R. P. Bell, *Proc. Roy. Soc.*, **A158**, 128 (1937).

The tunneling correction to the rates can now be calculated by combining eq 18 and 15; the result is

$$Q = \exp(E/\mathrm{k}T) \int_0^{\infty} (1/\mathrm{k}T) \exp[-(W/\mathrm{k}T) - \beta + (\beta W/E)]\, \mathrm{d}W \quad (19)$$

The advantage of the parabolic barrier is now apparent: it is that the expression for G is an exponential, which can easily be combined with the exponential term in eq 15 to give an expression that can be integrated directly. The result comes out to

$$Q = \frac{e^{\alpha}}{\beta - \alpha}(\beta e^{-\alpha} - \alpha e^{-\beta}) \quad (20)$$

where $\alpha = E/\mathrm{k}T$ and $\beta = 2\pi^2 a(2mE)^{1/2}/h$. In systems of interest to chemical kinetics, α and β are both in the range 10–40, so that $e^{-\alpha}$ and $e^{-\beta}$ are both small. For many systems of interest, $\alpha < \beta$ and eq 20 approximates to

$$Q = \beta/(\beta - \alpha) \text{ or } 1/Q = 1 - (\alpha/\beta) \quad (21)$$

The deviation of the rate from the value calculated for zero tunnel effect thus depends on α/β, which is

$$\alpha/\beta = hE^{1/2}/2\pi^2 a\mathrm{k}T(2m)^{1/2} \quad (22)$$

The deviation thus depends on the mass, the temperature, and the factor $E^{1/2}/a$ which is determined by the barrier dimensions. This factor $E^{1/2}/a$ is related to the curvature of the barrier at the top, which we will call c_t and is easily shown to be $2E/a^2$. Equation 22 may therefore be rewritten

$$\alpha/\beta = c_t^{1/2}h/4\pi^2 mT \quad (23)$$

This equation shows that the correction to the rate increases with increase of the curvature c_t and decrease of the mass m.

The curvature at the top may also be related to a frequency ν_t defined by

$$h\nu_t/\mathrm{k}T = 2\pi\alpha/\beta \text{ or } \nu_t = E^{1/2}/\pi a(2m)^{1/2} \quad (24)$$

whence

$$\nu_t = c^{1/2}/2\pi m^{1/2} \quad (24a)$$

This is easily shown to be the frequency with which a particle of mass m would execute a simple harmonic oscillation in a parabolic potential-energy well having the same curvature as the barrier—the mirror image of the barrier, so to speak. (Motion along the reaction coordinate may be said to correspond to an imaginary frequency, $i\nu_t$.) The correction to the rate evidently increases with increase of ν_t and decrease of the mass. The numerical values of c_t and ν_t are useful as quantitative measures of the degree of tunneling.

Another consequence of the expression 21 for Q is that the observed energy of activation, given by eq 3, comes out in terms of the barrier height E as

$$E_{\mathrm{obsd}}/E = 1 - [1/(\beta - \alpha)] \quad (25)$$

It is evident that E_{obsd} is less than E, and that the difference is greater the smaller is β, *i.e.*, the smaller are a and m. The observed A factor in the Arrhenius equation comes out in terms of the true A factor as

$$A_{\mathrm{obsd}}/A = [\beta/(\beta - \alpha)] \exp[-E/\mathrm{k}T(\beta - \alpha)] \quad (26)$$

The exponential term shows that A_{obsd} is less than A and is smaller the smaller are a and m.

To summarize, the rate, the apparent energy of activation, and the A factor all deviate from the values that would be calculated if the permeability of the barrier were zero, and the deviations increase with decrease of the mass and decrease of the barrier width (increase of the curvature at the top). These are the features that were pointed out in the Introduction and illustrated by the Arrhenius plots in Figure 5 and the derived plots in Figure 6.

The treatment was extended in a later paper[18] to unsymmetrical parabolic barriers, corresponding to reactions with a finite heat of reaction. The tunneling correction is necessarily smaller when there is a large energy difference between the initial and final states, since no tunneling can take place from systems with energies lower than the higher of these states. For small heats of reaction, of the order of 1 kcal mole^{-1}, the effect is not great, but for large heats of reaction it may become important. This is also shown by computations on unsymmetrical Eckart barriers.[14a] The plots in Figures 5 and 6 were actually calculated for a value of ΔH = 1 kcal mole^{-1}; for $Q = 0$, the results would be practically unchanged when $2a$ = 1.5 Å, but with $2a$ = 1.0 Å the value of $A^{\mathrm{D}}_{\mathrm{obsd}}/A^{\mathrm{H}}_{\mathrm{obsd}}$, for example, would be 50% higher.

2. *Bell's Later Treatment*

In a more recent treatment,[19,20] Bell gives a different solution for the permeability of a symmetrical parabolic barrier. In place of eq 18, he obtains

$$G(W) = [1 + \exp(\beta\gamma)]^{-1} \quad (27)$$

where $\gamma = 1 - (W/E)$. This equation turns out to be exact for parabolic barriers.[20] It differs in form from the previous equation (eq 18). Some values of the permeability calculated from it, with various values of β, are shown in Figure 3b. They show that there is a finite probability of penetration of the barrier ($G > 0$) when $W < E$, and also that there is partial "reflection" when $W > E$. It may be noted that $G = ½$ at $W = E$, a result that agrees with the value calculated from the Eckart barrier.[17]

The expression for $G(W)$ in eq 27, like the earlier one, has a form that allows it to be easily combined with the exponential term in eq 15 from which the rate of reaction is calculated. One obtains for the tunneling correction factor Q

$$Q = \int_{\infty}^{1} \frac{\alpha \exp(\alpha\gamma)\, \mathrm{d}\gamma}{1 + \exp(\beta\gamma)} \quad (28)$$

To integrate the equation, we first substitute $x = \exp(\alpha\gamma)$, so that

$$Q = \int_0^{e^{\alpha}} \frac{\mathrm{d}x}{1 + x^{\beta/\alpha}} = \int_0^{\infty} \frac{\mathrm{d}x}{1 + x^{\beta/\alpha}} - \int_{e^{\alpha}}^{\infty} \frac{\mathrm{d}x}{1 + x^{\beta/\alpha}} \quad (29)$$

The first integral is $(\pi\alpha/\beta)/\sin(\pi\alpha/\beta)$; the second can be expressed as a series

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(18) R. P. Bell, *Proc. Roy. Soc.*, **A154**, 414 (1936).

(19) R. P. Bell, *Trans. Faraday Soc.*, **54**, 1 (1959)

(20) R. P. Bell, ref 2, Chapter 11.

$$Q = \frac{\pi\alpha/\beta}{\sin \pi\alpha/\beta} - \frac{\alpha \exp(\alpha - \beta)}{\beta - \alpha}\left\{1 - \frac{\beta - \alpha}{2\beta - \alpha}\exp(-\beta) + \frac{\beta - \alpha}{3\beta - \alpha}\exp(-2\beta) - \ldots\right\} \quad (30)$$

This can be simplified when $\alpha < \beta$, which is commonly the case in problems of kinetic interest. Then $e^{\alpha} \ll e^{\beta}$, and $\exp(\alpha - \beta) \ll 1$, and all but the first term in (30) can be neglected. (This should, however, be verified in each case; in some calculations the second term is not negligible.) The result then takes the simple form

$$Q = (\pi\alpha/\beta)/\sin (\pi\alpha/\beta) \quad (31)$$

It is convenient to define a quantity u such that

$$u = 2\pi\alpha/\beta = h\nu_t/\mathbf{k}T = h/\pi a(2m/E)^{1/2}\mathbf{k}T \quad (32)$$

Then eq 31 may be written very simply as

$$Q = \tfrac{1}{2}u/\sin \tfrac{1}{2}u \quad (33)$$

Equation 33 differs entirely in form from the previous eq 21, but the numerical values calculated from it are often not greatly different. A direct comparison of the two treatments has been made for one reaction where the results indicate appreciable tunneling (see ref 61 and section IV.A.3.a). The results agree closely; the largest difference in barrier height is less than 0.1 kcal mole^{-1}, and for the barrier width it is 0.05 Å.

A more accurate expression than eq 33, taking into account the second term of the series, is (for $u < 2\pi$)

$$Q = \frac{\tfrac{1}{2}u}{\sin \tfrac{1}{2}u} - \frac{u}{2\pi - u}\exp\left\{-\frac{E}{\mathbf{k}T}\frac{(2\pi - u)}{u}\right\} \quad (33a)$$

This is accurate enough for any reaction so far studied. It may be noted in passing that eq 33 extends the relation between penetration of a parabolic barrier and oscillation in a parabolic well, since if we replace ν_t by $i\nu_t$ we obtain $Q = {}^1/_2u/(\sinh {}^1/_2u)$, which is the quantum correction for a real harmonic frequency in the transition state.[20]

The important general result is that the tunneling correction depends, as before, on the value of α/β, or of ν_t (eq 24), and therefore on the mass and on the factor $E^{1/2}/a$, which depends on the dimensions of the energy barrier.

We can now derive expressions for the apparent activation energy and A factor in terms of u. Using eq 3, we obtain from eq 33

$$E_{\text{obsd}} - E = \mathbf{k}T(\tfrac{1}{2}u \cot \tfrac{1}{2}u - 1) \quad (34)$$

$$A_{\text{obsd}}/A = (\tfrac{1}{2}u/\sin \tfrac{1}{2}u)\exp(\tfrac{1}{2}u \cot \tfrac{1}{2}u - 1) \quad (35)$$

As in the earlier treatment, E_{obsd} is less than E, and A_{obsd} is less than A, and the differences are greater the larger is α/β, *i.e.*, the smaller are m and a.

The values of E_{obsd} and A_{obsd} vary with temperature and with isotopic substitution in the same general way as those calculated by the earlier approximate eq 25 and 26 and represented in Figures 5 and 6. The general consequences in chemical kinetics have already been outlined. The results of detailed applications of these equations to various reactions in solution will be dealt with in section IV. Earlier calculations were done by hand and brain, but more recently computers have been used (see ref 66 and 75); this allows many more values of the barrier parameters to be tried and improves the accuracy of the fit.

Some comparisons of the quantitative predictions of this treatment with those calculated from the one-dimensional Eckart barrier have been made.[21] For the reaction H + H_2, the correction factor Q predicted at 500°K is about twice that for the Eckart barrier, but at 1000° the two treatments agree.[10] Much the same is true for the reaction between CF_3 and CHD_3 (see section III, ref 33). The parabolic barrier would be expected to overestimate tunneling at low temperatures, where most of the protons are of low energy, corresponding to the lower part of the barrier where it is narrower than an Eckart barrier. The relative figures for a series of related reactions should nonetheless be significant.

A one-dimensional barrier intermediate between the Eckart and parabolic barriers has been treated by Christov.[21] Mention should also be made of the earliest solution by Wigner[22] of the problem for a parabolic barrier; the result was an approximation valid only for very small tunneling corrections, but of interest in relation to later work.[20]

Values of the computed barrier dimensions for various reactions in solution are collected and discussed in section IV.B.

III. Tunneling in Reactions in the Gas Phase

Our main topic is reactions in solution, and we shall only deal briefly with reactions in the gas phase. Most of the work has been concerned with isotope effects. These are often conveniently determined by competition methods. The value of $A^{\text{D}}{}_{\text{obsd}}/A^{\text{H}}{}_{\text{obsd}}$, for instance, has been determined for the abstraction of H or D by CH_3, CD_3, or CF_3 radicals from a variety of molecules including H_2, HC_4, C_2H_6, CH_3COCH_3, C_2H_5OH, and their deuterated analogs. The technique is to produce methyl radicals, for example, by photolysis of acetone, in a mixture of (say) $C_2H_6 + C_2D_6$, and determine by mass spectrometry the relative amounts of CH_3H and CH_3D in the product. Measurements are made over a range of temperature and the value of $A^{\text{D}}{}_{\text{obsd}}/A^{\text{H}}{}_{\text{obsd}}$ obtained. This is commonly slightly greater than unity; thus for acetone it is 1.5 ± 0.1, and for ethane it is 3.5 ± 1.5. The deviations from unity, though small, are greater than the experimental errors and are in the direction expected for tunneling.[23–27] The largest deviation[28] (which, however, includes a small secondary isotope effect) is shown by the reaction $CD_3 + CD_4$ compared with $CH_3 + CH_4$; here $A^{\text{D}}{}_{\text{obsd}}/A^{\text{H}}{}_{\text{obsd}}$ is about 10, and $E^{\text{D}}{}_{\text{obsd}} - E^{\text{H}}{}_{\text{obsd}}$ is 3.5 kcal mole^{-1}. The corresponding abstraction reactions from N–H bonds do not show detectable tunneling effects.[29,30]

Interesting evidence is provided by the theoretical treatment of the abstraction reactions of CH_3 radicals with ethane and acetone, by Johnston and Rapp.[10,11] These authors used a potential-energy surface of the Sato type and derived values

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(21) S. G. Christov, *Ann. Phys.*, [7] **12**, 20 (1963); Proceedings of the 1st Australian Conference on Electrochemistry, Oxford, Pergamon Press, New York, N. Y., 1964, p 723; *Discussions Faraday Soc.*, **39**, 60 (1965).

(22) E. P. Wigner, *Z. Physik. Chem.*, **B19**, 903 (1932).

(23) J. R. McNesby and A. S. Gordon, *J. Amer. Chem. Soc.*, **76**, 823, 1416 (1954); **77**, 4719 (1955); **78**, 3570 (1956).

(24) R. Klein, J. R. McNesby, M. D. Scheer, and L. J. Schoen, *J. Chem. Phys.*, **30**, 58 (1959).

(25) J. R. McNesby, M. D. Scheer, and R. Klein, *ibid.*, **32**, 1814 (1960).

(26) J. R. McNesby, *J. Phys. Chem.*, **64**, 1671 (1960).

(27) P. Gray and A. A. Herod, *Trans. Faraday Soc.*, **64**, 1568 (1968).

(28) G. A. Creak, F. S. Dainton, and K. J. Ivin, *ibid.*, **58**, 326 (1962).

(29) P. Gray and J. Thynne, *ibid.*, **59**, 2275 (1963); **60**, 1047 (1964).

(30) P. Gray and J. C. Thynne, Tenth Symposium on Combustion, Combustion Institute, 1965, p 435.

of k^H/k^D, using the equations of transition-state theory and assuming (i) no tunnel effects, (ii) tunneling through a one-dimensional Eckart barrier, corresponding to a single reaction path, and (iii) tunneling also along other parallel reaction paths near the saddle (see section II.A.3). Figure 9 shows the comparison between these calculations and the experimental results[23,24,26,31,32] over a wide range of temperature. The best agreement is with the full treatment (iii); if tunneling is ignored the discrepancy is considerable. The same is true for the abstraction reaction of CF_3 radicals with CHD_3, which has been studied over the range from 300 to 1800°. If no tunneling correction is applied, the experimental results deviate from those calculated from the theoretical Sato potential-energy surface by a factor which increases as the temperature falls, to about 3 at 300°K. According to the authors this effect is much too large to be accounted for by any combination of uncertainties in the experiments or the theory.[33] The discrepancy is greatly reduced if a correction based on Bell's equations is introduced and still more if the many-path treatment of Johnston and Rapp is used. The authors conclude that the isotope effect cannot be understood without taking tunneling into account. These comparisons between theory and experiment are striking, but it should be remembered that they do not test the equations for tunneling alone, but a combination of those equations with particular potential-energy surfaces.

Isotope effects in the reactions of halogen atoms with simple molecules have been studied in much the same way. The reaction $Cl + H_2$ is the rate-determining step of the Nernst chain mechanism for the hydrogen–chlorine reaction. It was investigated[34] by producing chlorine atoms photochemically from Cl_2 in the presence of a mixture of hydrogen isotopes and determining the isotopic composition of the residual hydrogen, either by mass spectrometry (H_2, D_2, HD) or by radiochemical methods (HT, DT, T_2). The Arrhenius plots over the range -30 to $+70°$ were linear within experimental error, and the isotopic A factor ratios such as A^H/A^D were all somewhat greater than unity, showing no detectable tunneling effect. Comparison with the predictions of a transition-state treatment using a Sato-type potential-energy surface shows, however, that when all tunneling corrections are omitted from the calculations the values for the isotope effect are too small; with corrections based on the one-dimensional Eckart treatment, the values are too large, but agreement within 15% is obtained with the Johnston–Rapp treatment. (For the reaction $Br + H_2$, agreement is less satisfactory,[35] and for $I + H_2$ it was found impossible to adjust the Sato parameter to give agreement.[36]) We are again left with rather indirect evidence that a tunneling correction is needed in these reactions.

The deuterium isotope effect in the reaction $Cl + HCl \rightarrow ClH + Cl$ gives somewhat more positive evidence. It was investigated[37] by measuring the relative rates of exchange of radioactive chlorine in an irradiated isotopic mixture, by a competitive method, at 39.3, 95, and 150°. The experimental plot of log (k^H/k^D) against $1/T$ is curved, in the direction expected for tunneling, and deviates from the line calculated by transition-state theory from a Sato potential-energy surface without tunneling. A tunneling correction calculated by the method of Johnston and Rapp does not produce agreement, but the results are compatible with the simple Eckart treatment. The best agreement, however, is found for the Bell parabolic barrier.

To summarize the evidence from gas-phase reactions, we may say that there is little doubt that in several reactions kinetic isotope effects occur which are anomalous unless tunneling is taken into account, though the effects on k^H/k^D are within a factor of 10 even when the temperature range is several hundred degrees. There are a few cases where the Arrhenius plot is nonlinear or where A^H is less than A^D. These effects are less striking than those observed for reactions in solution (below). This is in part because gas reactions are commonly studied at relatively high temperatures, where tunneling is expected to be less important because more molecules have energies comparable with the height of the energy barrier.

IV. Tunneling in Reactions in Solution

A. EXPERIMENTAL WORK AND CALCULATIONS

1. Introduction

Although the first experimental results to show evidence pointing clearly to an important tunneling effect were not obtained until 20 years after Bell's calculations, there are now about a dozen instances of reactions in solution where tunneling seems the likeliest interpretation of the observations. As compared with the gas phase, the indications for reactions in solution are more striking, in that nonlinear Arrhenius plots and values of A^D/A^H much greater than unity are observed, and it would be difficult to give an alternative interpretation of a considerable body of data. On the other hand, no theoretical potential-energy surfaces are available for reactions in solution, and consequently no detailed comparisons have been made of the various theoretical treatments of tunneling. Most of the data have so far been analyzed only in terms of Bell's first approximation for a symmetrical parabolic barrier. That tunneling must be taken into account seems to be established, but the second phase, in which quantitative information about energy barriers may be expected, is only beginning. Each phase has difficulties to overcome; these may now be briefly noticed.

Alternative explanations of the observations must be ruled out before the interpretation in terms of tunneling can be regarded as convincing. Deviations from the Arrhenius equation can arise for various reasons quite unconnected with tunneling.[38,39] (i) One reason is a change of mechanism at low

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(31) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1954.

(32) F. O. Rice and T. A. Vanderslice, *J. Amer. Chem. Soc.*, **80**, 291 (1958).

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(36) J. H. Sullivan, *ibid.*, **39**, 3001 (1963).

(37) F. S. Klein, A. Persky, and R. E. Weston, *ibid.*, **41**, 1799 (1964).

(38) R. P. Bell, *Discussions Faraday Soc.*, **39**, 16 (1965).

(39) J. R. Hulett, *Quart. Rev.* (London), **18**, 227 (1964).

temperatures; if there are two concurrent reactions, the one with the higher activation energy will become dominant as the temperature rises, and the Arrhenius plot will curve in the same direction as for tunneling. It is therefore necessary to establish in each case that the same reaction is being studied over the whole temperature range.

(ii) Another reason is a change of solvation when the transition state is formed. This appears to be the interpretation of the slight dependence of the enthalpy of activation on temperature which is observed for many reactions in which the reactants are markedly less polar than the transition state.[39] Accurate rate measurements give curved Arrhenius plots, which can be analyzed in terms of the equation

$$\log k = -A/T + B \log T + C \tag{36}$$

which corresponds to a linear dependence of $\Delta H^{\ddagger}$ on temperature, implying a constant value of $\Delta C_p^{\ddagger} (= BR)$. The derived values of $\Delta C_p^{\ddagger}$ can be interpreted in terms of solvent orientation on forming the transition state. For some reactions, the possibility of such an interpretation can be ruled out because the effect would be in the wrong direction; for others, because it predicts a curvature throughout the temperature range and greater at high temperatures ($\propto T^2$), whereas the observed results follow a linear Arrhenius plot (within experimental error) at higher temperatures with a comparatively sharp deviation at the lower end of the range. Nonetheless, the form of the plot (and so the values deduced for the barrier dimensions) may be affected in this way by solvent reorientation.

(iii) A third possibility is that a change in the structure of the solvent at low temperatures might affect the Arrhenius plot.[39] In water, for instance, decrease of temperature leads to a more ordered structure, and so might lead to a less positive value of $\Delta S^{\ddagger}$ and a smaller A factor for reactions in which the transition state is less polar than the initial state. Such an effect, depending mainly on the properties of the solvent, is unlikely if different reactions show widely different tunneling effects in the same solvent, as is observed for various reactions in water and ethanol.

(iv) It has been pointed out by Hills that a curvature of the Arrhenius plot would result if the energy of activation at constant volume ($\Delta U_v^{\ddagger}$) were temperature independent, as the corresponding quantity for ion migration has been shown to be, rather than the enthalpy of activation at constant pressure ($\Delta H_p^{\ddagger}$) as normally measured.[40-44] The relation between the two quantities is

$$\Delta H_p^{\ddagger} = \Delta U_v^{\ddagger} + (\alpha T \Delta V_T^{\ddagger}/\beta) \tag{37}$$

where α and β are the coefficients of cubical expansion and compressibility; it follows that if $\Delta U_v^{\ddagger}$ were independent of temperature, $\Delta H_p^{\ddagger}$ would not be. In general the data for calculating $\Delta U_v^{\ddagger}$ by eq 37 from the observed values of $\Delta H_p^{\ddagger}$ are not available, since rates at high pressure are needed to evaluate $\Delta V_T^{\ddagger}$. A recent study[44] of the methanolysis of *t*-butyl chloride, for which $\Delta H_p^{\ddagger}$ varies with temperature (*cf.* (iii) above), showed that $\Delta U_v^{\ddagger}$ was about equally temperature dependent. There is indeed no reason to think that in chemical reactions, as distinct from ion migration, $\Delta U_v^{\ddagger}$ is a physically simpler quantity than $\Delta H_p^{\ddagger}$ or more directly related to conditions in the gas phase. When the transition complex is formed, in reactions where there is a marked change in polarity, there is a change in the orientation of solvent molecules, and consequently a change in volume, in the neighborhood of the complex. Under constant-pressure conditions, the structure and volume of the bulk of the solvent are unaltered, and the over-all result is a change in the volume of the solution. Under constant-volume conditions, the local volume change around the transition complex must be compensated by an equal and opposite volume change in the bulk solvent, brought about by a change in the external pressure; thus the structure of the bulk solvent is altered, as well as that near the transition complex, and the two effects may be difficult to disentangle; the value of $\Delta U_v^{\ddagger}$ may depend on the properties of the solvent at least as much as that of $\Delta H_p^{\ddagger}$.

(v) The possibility that during the process of forming the transition complex the reorientation of solvent molecules cannot keep pace with the transfer of the proton has been raised by Bell[38] and Kreevoy.[45] It has been noticed that the dielectric relaxation time for water, which is in the region of 10^{-11} sec, is probably greater than the time required for a proton transfer between two suitably oriented activated molecules, which may be estimated as 10^{-12}–10^{-13} sec. The resulting departure from equilibrium would be greater for proton transfer than for deuteron transfer, since the deuteron moves more slowly; and it would probably be greater at lower temperatures, since the reorientation of solvent molecules is slower. Thus both the effects predicted for tunneling might be simulated. This possibility of nonequilibrium behavior could be important for the general theory of reactions in solution; the interpretation of A factors, for instance, leans heavily on the view that solvent reorientation controls $\Delta S^{\ddagger}$ and hence A, and it is important to know whether reorientation may lag behind changes in bonding. Unfortunately, it is difficult to make any quantitative estimates, because of the lack of information about the time required for a proton transfer and the times involved in molecular motions near a polar transition state. The following considerations suggest, however, that nonequilibrium behavior is not the rule. (a) In the extreme case, solvent reorientation would become rate determining, and the energy of activation would have a value of a few kilocalories, comparable with that for viscosity or dielectric relaxation. There are indeed reactions where the activation energy has such values, but they are either very fast and diffusion controlled[46] or else involve the solvent as a reagent,[47] and this is not true of most of the reactions being considered. (b) The dielectric relaxation time is that required for a considerable cooperative motion of many solvent molecules. It appears that smaller motions can

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(44) G. J. Hills and C. A. Viana, Symposium on Equilibria and Reaction Kinetics in Hydrogen-Bonded Solvent Systems, Newcastle, England, 1968.

(45) M. M. Kreevoy and R. A. Kretchmer, *J. Amer. Chem. Soc.*, 86, 2435 (1964).

(46) E. F. Caldin, "Fast Reactions in Solution," Blackwell Scientific Publications, Chapter 12, 1964.

(47) H. Beens, K. H. Grellmann, M. Gurr, and A. H. Weller, *Discussions Faraday Soc.*, 39, 183 (1965).

occur in much shorter times, down to 10^{-13} sec.[48-50] (c) The effects might be expected to depend on the solvent and on the extent of reorientation, which is reflected in the value of $\Delta S^{\ddagger}$. It would therefore be predicted that a series of reactions in the same solvent with similar values of $\Delta S^{\ddagger}$ would show similar deviations from the Arrhenius equation (for example), and that reactions with a larger $\Delta S^{\ddagger}$ would show larger deviations. This behavior is not observed (see ref 92). Further information on this question, both experimental and theoretical, is much to be desired.

We turn now to the question of the reliance that can be placed on the quantitative data derived from experiments. Although the results which follow indicate that there is a considerable tunneling effect in several reactions, the numerical values derived for the barrier dimensions must be treated with some reserve, for the following reasons. (a) There is first the uncertainty inherent in the choice of the theoretical model. The actual potential-energy barrier is presumably more nearly bell-shaped than parabolic; the parabolic barrier is therefore too narrow at the base, with the result that it overestimates tunneling at the lower temperatures where most systems are in low-energy states. (b) Again, the model takes no account of other factors that may influence the isotope effect, such as bending vibrations in the transition state,[38] which partly compensate the tunneling correction. (c) There are the uncertainties introduced by approximations. In most of the calculations so far carried out, only the first approximation has been used (eq 31, 33–35). (d) Moreover, in all the calculations it has been assumed that the energy barrier is symmetrical, corresponding to a negligible heat of reaction. If ΔH° is not zero, the effect of tunneling on the rate is smaller (section II, p 142); consequently, if the rate measurements are analyzed by means of the equations for symmetrical barriers, the values obtained for the curvature of the barrier will be too small (*i.e.*, in general the barrier width will be too large). Unfortunately the values of ΔH° are not known for most of the reactions of interest. (e) The energy of activation is assumed to be attributable entirely to changes in bonds involving the proton. If solvation changes, or changes of configuration, contribute appreciably to the activation energy, the curvature of the barrier will again be underestimated.

There are thus several factors that may tend to reduce the curvature below its true value and so give too high a value for the barrier width, thereby partly cancelling the effect of the unrealistic shape of the barrier. The net effect of these influences cannot yet be estimated.

Despite all this, the relative values of the barrier dimensions derived for a series of related reactions may be expected to be significant. It is therefore worthwhile to carry out simple calculations on a consistent basis and compare the results.

The order of presentation in this review is as follows. The earlier work, up to 1955, is first summarized in section IV.A.2. The first investigation to give a clear indication of tunneling, published in 1956, is outlined in section IV.A.3; this work was on the isotope effect for a reaction between a ketone and a base. Isotope effects are next considered, first those for reactions between other ketones and bases, and then those for some hydride-ion transfers. Investigations showing deviations from linear Arrhenius plots are then dealt with (section IV.A.4). This order is not historical, except for the first few pages; the treatment is intended to show the present state of the evidence rather than the ways in which it was reached.

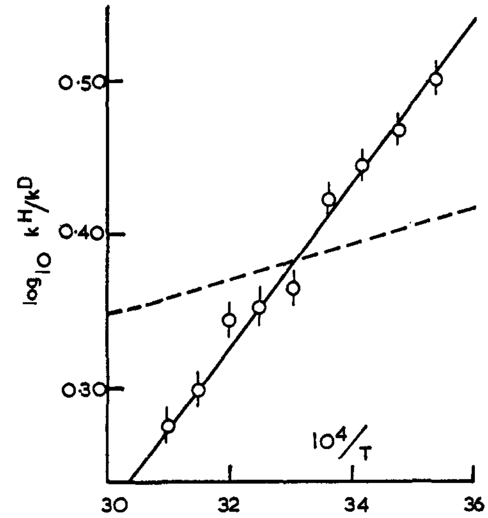

Figure 10. Plot of log (k^H/k^D) against $1/T$ for the reaction of 2-carbethoxycyclopentanone with fluoride ion in water: circles, experimental points; full line, best line by least squares; dashed line, slope calculated for $A^D_{obsd} = A^H_{obsd}$.

2. Earlier Work

The first definite indication that the tunnel effect was significant in controlling the rate of a reaction in solution was published in 1956. Before this a number of proton-transfer reactions had been investigated, by measuring either their isotope effects or their temperature coefficients down to low temperatures, without any positive indication being observed. These investigations may be summarized briefly.

Rate measurements on proton-transfer reactions at low temperatures were first made by Bell and his coworkers, who used a cryostat cooled by evaporation of liquid ammonia or sulfur dioxide, down to −40°. The bromination of acetone catalyzed by hydrogen chloride or bromide in aqueous acetone was studied[51] from +10 to −40°. The rate of ionization of nitroethane in aqueous methanol containing sodium hydroxide was measured[52] from +20 to −32°. For both reactions the Arrhenius equation was obeyed within experimental error. The temperature range was extended by Caldin and his coworkers by the use of solid carbon dioxide or liquid nitrogen as cooling agents. The reactions of ethoxide ion with trinitrophenylmethane and with 2,4,6-trinitrotoluene in ethanol–toluene solution were investigated[53,54] over the range +20

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(48) J. G. Powles and R. Figgins, *Mol. Phys.*, **10**, 155 (1966).

(49) R. A. Dwek and R. E. Richards, *Discussions Faraday Soc.*, **43**, 196 (1967).

(50) H. G. Hertz, *Ber. Bunsenges. Phys. Chem.*, **71**, 103, 979, 999, 1008, 1032 (1967).

(51) R. P. Bell and J. K. Thomas, *J. Chem. Soc.*, 1573 (1939).

(52) R. P. Bell and A. Norris, *ibid.*, 118, 854 (1941).

(53) E. F. Caldin and J. C. Trickett, *Trans. Faraday Soc.*, **49**, 772 (1953).

(54) E. F. Caldin and G. Long, *Proc. Roy. Soc.*, A228, 263 (1955).

to −80°; no deviation from the Arrhenius equation was observed.

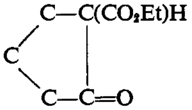
The deuterium isotope effect for the base-catalyzed decomposition of nitramide, a reaction which was known to be a particularly clean example of general base catalysis,[55–58] was studied by Bell and Caldin.[59] The base used was dimethylaniline and the solvent anisole. No anomaly was observed.

The failure to observe the characteristic effects of tunneling in these reactions was put down to the energy barrier being too wide for the effects to be detectable. Barrier widths of 1.5 Å would be enough. Since a barrier a few tenths of an ångström narrower would show appreciable tunneling, the investigations were continued, and positive results were eventually obtained.

3. *Isotope Effects*

a. The Base-Catalyzed Bromination of 2-Carbethoxycyclopentanone

An investigation by Bell, Fendley, and Hulett[60] on the deuterium isotope effect in the base-catalyzed bromination of 2-carbethoxycyclopentanone gave the first clear evidence of a detectable tunneling correction to a reaction rate. This reaction is a typical ketone halogenation; the reaction is catalyzed generally by bases, and the rate-determining step is a proton transfer


(RH)

$$+ X^- \longrightarrow HX + R^- \qquad (38)$$

The solvent used was D_2O, containing 0.2 *M* KBr. Exchange between the solvent and the substrate RH is slow, so that it was possible to follow the proton-transfer by doing the kinetic run immediately after making up a solution, and the deuteron transfer after leaving it for a day. The rate was determined by adding bromine solution from a microsyringe and measuring the time taken for the free bromine to disappear, by a sensitive conductometric method. The temperature was varied between 5 and 55°. By this simple technique it was possible to determine the rates and Arrhenius parameters for the two isotopic reactions, in the same solvent.

The catalysts used (X^-) were fluoride ion and monochloroacetate ion; the solvent also acts as a base catalyst. For all three, the values of $(A^D{}_{obsd}/A^H{}_{obsd})$ were greater than unity, and $(E^D{}_{obsd} - E^H{}_{obsd})$ greater than 1.1 kcal mole^{-1} (Table I). The largest effect is shown by fluoride catalysis, for which the value of $(A^D{}_{obsd}/A^H{}_{obsd})$ is 24 ± 4, a value differing from unity by much more than the limits of error. Figure 10 shows the experimental data, along with the line calculated on the assumption that the value is unity; it is evident that this is incompatible with the results.

The theoretical equations for a symmetrical parabolic barrier (eq 33–35) were fitted to the results. There are three unknowns: the width of the parabola, $2a$; the height for proton transfer, E^H; and that for deuteron transfer, E^D. (E^D will in general differ from E^H, by an amount that will depend on the zero-point energy in the transition complex but will lie between 0 and about 1.1 kcal mole^{-1}, the difference of zero-point energies of C–H and C–D bonds.) The experimental results provide three independent quantities, such as $A^D{}_{obsd}/A^H{}_{obsd}$, $E^H{}_{obsd}$, and $E^D{}_{obsd}$, so the values of a, E^H, and E^D can be determined. The results are given in Table I.

Table I

Arrhenius Parameters and Barrier Dimensions for the Base-Catalyzed Bromination of 2-Carbethoxycyclopentanone in D_2O[a]

	D_2O	CH_2ClCOO^-	F^-
Log $(A^D{}_{obsd}/A^H{}_{obsd})$	0.36 ± 0.05	0.46 ± 0.06	1.38 ± 0.07
$E^D{}_{obsd} - E^H{}_{obsd}$	1.21 ± 0.08	1.45 ± 0.08	2.44 ± 0.10
E^H	13.1_6 (13.2)	12.5_3 (12.5)	18.0 (18.0)
E^D	13.5_4 (13.6)	12.9_5 (12.9)	18.0_8 (18.0)
$E^H{}_{obsd}/E^H$	0.90	0.88	0.81
$E^D{}_{obsd}/E^D$	0.96	0.95	0.94
a	0.631 (0.604)	0.584 (0.563)	0.587 (0.583)

[a] E in kcal mole^{-1}; a in Å. E^H, E^D, and a are calculated[61] from Bell's 1959 equations;[19] the values in brackets are from his 1935 equations.[15,60]

Several points call for comment. (i) The observed energy of activation, which is a measure of the average excess energy of the reacting systems, is 80–90% of the height of the energy barrier; this indicates that the tunneling correction is not so large that the approximate formulas should not be used. (ii) The effect of the tunneling correction on the rate constant, which may be calculated from eq 21 or 33, is considerable; the rate is larger than it would be on the classical model, by a factor of up to 6. The value of k^H/k^D depends as much upon the different tunneling factors for H and D as upon the difference of zero-point energies. (iii) The values for the barrier width are of the order to be expected. For D_2O, for example, if we take the van der Waals radii of carbon and oxygen as 2.0 and 1.5 Å, the distance of closest approach of the centers without reaction is 3.5 Å; with the usual bond lengths, the distance over which the proton is transferred is about 1.3 Å. (iv) The barrier width found for F^- is slightly greater than for monochloroacetate, so the larger tunnel effect for F^- must be attributed to the larger value for the barrier height, which leads to a greater curvature of the barrier and hence to a higher permeability. (v) For fluoride catalysis $E^D - E^H$ is zero (±0.2 kcal mole^{-1}). This implies that the difference of zero-point energies for H and D in the transition complex is much the same as that in the initial state. This zero-point energy could not, of course, be due to a symmetrical stretching vibration, but it could be due to an unsymmetrical stretching vibration; or, alternatively, it could be due to a bending vibration, with a frequency of 1200–1600 cm^{-1} (comparable with that for the ion HF_2^-), indicating a considerable "stiffness" in the transition complex. Such results are of the greatest interest for our knowledge of energy barriers and of the structures of transition complexes.

The Arrhenius plot for the fluoride-catalyzed proton trans-

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(55) J. N. Brønsted, *Chem. Rev.*, 5, 322 (1928).

(56) J. N. Brønsted and H. C. Duus, *Z. Physik. Chem.*, 117, 299 (1929).

(57) J. N. Brønsted and J. E. Vance, *ibid.*, A163, 240 (1933).

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(59) R. P. Bell and E. F. Caldin, *Trans. Faraday Soc.*, 47, 50 (1951).

460) R. P. Bell, J. A. Fendley, and J. R. Hulett, *Proc. Roy. Soc.*, A235 (53 (1956).

fer should deviate from linearity at a temperature not much below 0°, according to a calculation made from the parabolic-barrier model with the above dimensions. The temperature at which $E^{\mathrm{H}}{}_{\mathrm{obsd}}/E^{\mathrm{H}}$ falls to $^1/_2$ can be estimated by considering the special case[18] $\alpha = \beta$, for which $E_{\mathrm{obsd}}/E = {}^1/_2\beta/(\beta + 1)$. For reactions of practical interest $\beta \gg 1$, so the condition for $E_{\mathrm{obsd}}/E = {}^1/_2$ is $\alpha = \beta$, whence $T = hE^{1/2}/2\pi^2 a\mathrm{k}(2m)^{1/2}$. For fluoride ion the data in Table I give $T = -20°$. To work at this temperature, Hulett[61] used a 5.2 *M* aqueous solution of sodium bromide and was able to measure rates of reaction from +25 to −20°. The Arrhenius plot showed a curvature in the expected direction; the rate constant at −20° was 75% above the value corresponding to a linear plot. However, this result is less impressive as a confirmation of the isotope work than it appears at first sight. In a solution as concentrated as 5.2 *M*, in which the ratio of H_2O molecules to ions is only about 5, we should expect large kinetic salt effects and much ion pairing. The salt concentration has a marked influence on the rates of such reactions and the Arrhenius parameters.[62] Moreover, a curved Arrhenius plot that cannot be attributed to tunneling was obtained by Hulett[63] for a related reaction in a concentrated aqueous solution. He measured the rate of bromination of acetone in the presence of hydroxide, where the rate-determining step is the proton transfer from acetone to OH^-, and used 6.7 *M* sodium perchlorate in order to work over a temperature range down to −25°. He found that the Arrhenius plot was curved not only for proton transfer but for deuteron transfer as well. This result he ascribed to a medium effect, specific to hydroxide ion in water. Later work by Jones[64] on the reaction of acetone with OH^- in concentrated salt solutions showed that the tritium isotope effect ($k^{\mathrm{T}}/k^{\mathrm{H}}$) varied with concentration, in a way that might be explained by ion pairing; it was suggested that this might account for the nonlinear Arrhenius plot. These anomalies may be peculiar to reactions of hydroxide ions, but they suggest that further elucidation of salt effects is needed before reliance can be placed on the curved Arrhenius plot for the reaction of fluoride ion with 2-carbethoxycyclopentanone.

There is no doubt, however, about the cogency of the evidence from the isotope effect. It is of interest that in 1959 this was the only proton-transfer reaction for which there was good evidence for tunneling. All the rest of the present considerable body of evidence, considered below, has been published in the last 10 years.

b. The Deuterium and Tritium Isotope Effects in the Reactions of Hydroxide Ion with Acetone and Diisopropyl Ketone in Water

Measurements of the deuterium and tritium isotope effects in the reaction of acetone with OH^- were made by Jones,[65] at concentrations where the complications mentioned above should not be relevant. The Arrhenius parameters, recalculated from Jones' results,[66] give a large difference of activation energies ($E^{\mathrm{D}}{}_{\mathrm{obsd}} - E^{\mathrm{H}}{}_{\mathrm{obsd}} = 2.4 \pm 0.3$ kcal mole^{-1}) and a value for $\log(A^{\mathrm{D}}{}_{\mathrm{obsd}}/A^{\mathrm{H}}{}_{\mathrm{obsd}})$ of 0.8 ± 0.2, corresponding to a value of $A^{\mathrm{D}}{}_{\mathrm{obsd}}/A^{\mathrm{H}}{}_{\mathrm{obsd}}$ of about 6. These values indicate an appreciable tunneling effect. Application of Bell's equations for a symmetrical parabolic barrier gives the best fit with barrier heights $E^{\mathrm{H}} = 13.6$ and $E^{\mathrm{D}} = 14.7$ kcal mole^{-1}, and width $2a = 1.260$ Å. The results with tritium appear difficult to interpret[65] (see also ref 8) and were not analyzed.

Table II

Tritium Isotope Effect and Barrier Dimensions for the Reactions of OH^- with *o*- and *p*-Methoxyacetophenone in Water[a]

	o-Methylacetophenone	*p-Methoxyacetophenone*
$E^{\mathrm{T}}{}_{\mathrm{obsd}}$	15.5 ± 0.3	17.1 ± 0.3
$E^{\mathrm{H}}{}_{\mathrm{obsd}}$	11.86 ± 0.08	13.8 ± 0.6
$E^{\mathrm{T}}{}_{\mathrm{obsd}} - E^{\mathrm{H}}{}_{\mathrm{obsd}}$	3.6 ± 0.4	3.3 ± 0.9
Log $(3A^{\mathrm{T}}{}_{\mathrm{obsd}}/A^{\mathrm{H}}{}_{\mathrm{obsd}})$	1.5 ± 0.26	1.1 ± 0.6
$3A^{\mathrm{T}}{}_{\mathrm{obsd}}/A^{\mathrm{H}}{}_{\mathrm{obsd}}$	32	12
E^{T}	15.5	17.1
E^{H}	14.1	15.9
$2a$	1.270	1.216

[a] *E* in kcal mole^{-1}; *a* in Å.

For diisopropyl ketone, $CO(CHMe_2)_2$, the position is less clear. The tritium isotope effect[67] indicates a value of $A^{\mathrm{T}}{}_{\mathrm{obsd}}/A^{\mathrm{H}}{}_{\mathrm{obsd}}$ close to unity, indicating that the tunnel effect is small, although the Arrhenius plot for the proton transfer[68] over the range 0–50° showed a deviation from linearity in the right direction. The plot can, however, be regarded as being made up of two straight lines meeting at about 30°, whereas the theoretical equations give a smooth curve.[66] It seems possible that the change in slope may be due to a change in mechanism; further work is needed to decide this.

c. The Tritium Isotope Effect in the Reactions of Hydroxide Ion with Substituted Acetophenones in Water

Acetophenone and its substituted derivatives react with OH^- in the same way as acetone. Jones and his colleagues have measured the rates of the proton-transfer reactions by bromination and those of the triton-transfer reactions by detritiation.[69] A considerable tunnel effect is shown by the reactions of *o*-methylacetophenone, where the ratio of the *A* factors is around 30; and of *p*-methoxyacetophenone, where it is about 12. (A statistical factor of 3 is introduced, since in the experiments there are three ionizable protons but only one ionizable triton per molecule; thus the relevant ratio is $3A^{\mathrm{T}}{}_{\mathrm{obsd}}/A^{\mathrm{H}}{}_{\mathrm{obsd}}$.) The best values of the Arrhenius parameters and parabolic-barrier dimensions[66] are shown in Table II.

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(61) J. R. Hulett, *Proc. Roy. Soc.*, **A251**, 274 (1959).

(62) J. R. Hulett, *Trans. Faraday Soc.*, **59**, 1815 (1963).

(63) J. R. Hulett, *J. Chem. Soc.*, 1166 (1965).

(64) J. R. Jones and S. C. Subba Rao, *Trans. Faraday Soc.*, **63**, 111 (1967).

(65) J. R. Jones, *ibid.*, **61**, 95 (1965).

(66) E. F. Caldin and G. Tomalin, *ibid.*, **64**, 2823 (1968).

(67) J. R. Jones, *ibid.*, **61**, 2456 (1965).

(68) J. R. Hulett, *J. Chem. Soc.*, 430 (1965).

(69) J. R. Jones, R. E. Marks, and S. C. Subba Rao, *Trans. Faraday Soc.*, **63**, 993 (1967).

d. The Deuterium and Tritium Isotope Effects in the Reactions of Pyridine Bases with 2-Nitropropane in *t*-Butyl Alcohol–Water

The rate-determining step in the iodination of 2-nitropropane catalyzed by pyridine bases[70] is the proton transfer

$$(\mathrm{CH_3})_2\mathrm{CHNO_2} + \mathrm{py} \longrightarrow (\mathrm{CH_3})_2\mathrm{C}\cdot\mathrm{NO_2}^- + \mathrm{pyH}^+$$

The deuterium isotope effect was measured for a series of bases in aqueous *t*-butyl alcohol, in which the reaction is uncomplicated, by Lewis and Funderburk.[71] The value of $k^{\mathrm{H}}/k^{\mathrm{D}}$ at 25° is about 10 for pyridine and for various substituted pyridines, so long as one of the hydrogen atoms adjacent to the nitrogen atom remained unsubstituted; but for 2,6-dimethylpyridine and 2,4,6-trimethylpyridine it rises to 24, a value well above the limit set by classical theory. The corresponding value of the tritium isotope effect $k^{\mathrm{H}}/k^{\mathrm{T}}$ was later shown[8,72] to be 78 ± 4, a value in accord with Swain's equation.[7] Lewis notes that this agreement tells against the hypothesis that the large deuterium isotope effect is due to some mechanistic complication resulting in an addition of several normal isotope effects. The temperature coefficient of $k^{\mathrm{H}}/k^{\mathrm{D}}$ was measured for the reaction with 2,4,6-trimethylpyridine over a rather small range (20–32°); the value of $E^{\mathrm{D}}_{\mathrm{obsd}} - E^{\mathrm{H}}_{\mathrm{obsd}}$ is 3.0 kcal mole^{-1} and that of log $(A^{\mathrm{H}}_{\mathrm{obsd}}/A^{\mathrm{D}}_{\mathrm{obsd}})$ is -0.16, whence $A^{\mathrm{D}}_{\mathrm{obsd}}/A^{\mathrm{H}}_{\mathrm{obsd}}$ is about 7. These values indicate a considerable tunneling correction. The computed best values of the parabolic-barrier dimensions[66,73] are $E^{\mathrm{D}} = 17.6$ kcal mole^{-1}, $E^{\mathrm{H}} = 16.3$ kcal mole^{-1}, and $2a = 1.14$ Å.

It was this work that first suggested that tunneling might be exceptionally prominent in sterically hindered reactions. The two bases for which the isotope effects are unusually large are the only two of the series which are 2,6-substituted, so that access to the nitrogen is hindered. That this steric hindrance is enough to alter the rates of proton-transfer reactions considerably is shown by the Brønsted plot; the rates for these two bases are about one-fifth as fast as would be expected from those for other bases. We can understand, moreover, how tunneling might be favored in such reactions. Steric hindrance implies that there is repulsion between the incoming molecule and the methyl groups adjacent to the nitrogen atom to which the proton migrates. Consequently the potential-energy barrier will have a contribution from steric repulsion energy, as well as from the energy required to stretch the C–H bond. At short interatomic distances the repulsive energy between atoms rises rapidly as the distance decreases. The barrier will therefore be exceptionally steep near the top. The curvature at the top will be unusually large, and this will be reflected in a high tunneling factor (*cf.* section II.B).

e. The Deuterium and Tritium Isotope Effects in the Reaction of Ethoxide Ion with 1-Bromo-2-phenylpropane ($\mathrm{PhMeCHCH_2Br}$) in Ethanol

1-Bromo-2-phenylpropane when treated with sodium ethoxide in ethanol undergoes an elimination reaction whose rate-determining step is a proton transfer from the 2-carbon atom.

$$\mathrm{PhMeCHCH_2Br} + \mathrm{OEt}^- \longrightarrow \mathrm{PhMeC{=}CH_2} + \mathrm{Br}^- + \mathrm{EtOH}$$

The rates of this reaction and of the corresponding deuteron transfer were measured[74] over a temperature range from 5 to 55°. The value of $k^{\mathrm{H}}/k^{\mathrm{D}}$ at 25° is about 7 and increases as the temperature falls. The Arrhenius parameters give $E^{\mathrm{D}}_{\mathrm{obsd}} - E^{\mathrm{H}}_{\mathrm{obsd}} = 1.77 \pm 0.12$ kcal mole^{-1} and $A^{\mathrm{D}}_{\mathrm{obsd}}/A^{\mathrm{H}}_{\mathrm{obsd}} = 2.53 \pm 0.3$. These values indicate an appreciable degree of tunneling. When Bell's equations for a symmetrical parabolic barrier are applied to them, the barrier width (to which the calculations are most sensitive) comes out as 1.589 Å. (This is notably larger than for the reactions previously considered, which were all in aqueous solution; *cf.* section IV.B.) The difference in barrier heights $E^{\mathrm{D}} - E^{\mathrm{H}}$ is 0.90 kcal mole^{-1}, comparable with the difference in zero-point energy of the C–H and C–D bonds.

The tritium isotope effect was later investigated by Shiner and Martin,[75] who used a competitive method in which k^{T} was compared with k^{D}. The Arrhenius parameters gave $E^{\mathrm{T}}_{\mathrm{obsd}} - E^{\mathrm{D}}_{\mathrm{obsd}} = 0.68 \pm 0.025$ kcal mole^{-1} and $A^{\mathrm{T}}_{\mathrm{obsd}}/A^{\mathrm{D}}_{\mathrm{obsd}} = 1.19 \pm 0.04$. These values are much closer to the classical values (0 and 1) than are those for the deuterium isotope effect, but the deviations are outside the experimental error and are the first experimental indication that deuterium can show an appreciable tunnel effect in chemical kinetics, though a much smaller one than H. When the parabolic-barrier model was applied, the results were in excellent agreement with those from the deuterium isotope effect; in particular the value of the barrier width came out to almost the same value, 1.592 Å. The results are summarized in Table III.

Table III

Deuterium and Tritium Isotope Effects and Barrier Dimensions for the Reaction of Ethoxide Ion with 1-Bromo-2-phenylpropane in Ethanol[a]

	From H–D effect	*From D–T effect*
$E^{\mathrm{H}}_{\mathrm{obsd}}$	20,655 ± 74	. . .
$E^{\mathrm{D}}_{\mathrm{obsd}} - E^{\mathrm{H}}_{\mathrm{obsd}}$	1,766 ± 115	. . .
$E^{\mathrm{T}}_{\mathrm{obsd}} - E^{\mathrm{D}}_{\mathrm{obsd}}$	. . .	679.4 ± 25
Log $(A^{\mathrm{D}}_{\mathrm{obsd}}/A^{\mathrm{H}}_{\mathrm{obsd}})$	0.4035 ± 0.05	. . .
$A^{\mathrm{D}}_{\mathrm{obsd}}/A^{\mathrm{H}}_{\mathrm{obsd}}$	2.53 ± 0.3	. . .
Log $(A^{\mathrm{T}}_{\mathrm{obsd}}/A^{\mathrm{D}}_{\mathrm{obsd}})$	. . .	0.0744 ± 0.014
$A^{\mathrm{T}}_{\mathrm{obsd}}/A^{\mathrm{D}}_{\mathrm{obsd}}$	. . .	1.19 ± 0.04
E^{T}	. . .	23,447
E^{D}	23,003	22,961
E^{H}	22,099	. . .
$2a$	1.589	1.592

[a] E in cal mole^{-1}; a in Å.

This was the earliest work in which the tritium and deuterium isotope effects were determined for the same reaction, and the two values for the tunneling corrections could be compared. Although the tunneling factors are not among the largest known, the agreement between the independent values for the barrier dimensions is striking.

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(70) E. S. Lewis and J. D. Allen, *J. Amer. Chem. Soc.*, **86**, 2022 (1964).

(71) E. S. Lewis and L. H. Funderburk, *ibid.*, **89**, 2322 (1967).

(72) Dr. R. E. Davis reports (personal communication) that this value was not confirmed in experiments by a competitive method. Such methods, however, are less suitable the larger the rate ratio. Bell and Goodall[97] found that in water at 25° the ratio $k^{\mathrm{H}}/k^{\mathrm{D}}$ is 19.5, comparable with Lewis and Funderburk's value.

(73) R. M. Hyde, personal communication.

(74) V. J. Shiner and M. L. Smith, *J. Amer. Chem, Soc.*, **83**, 593 (1961).

(75) V. J. Shiner and B. Martin, *Pure Appl. Chem.*, **8**, 371 (1964).

f. The Deuterium Isotope Effect in the Reaction of Ethoxide Ion with 4-Nitrobenzyl Cyanide in Ethanol–Ether

4-Nitrobenzyl cyanide reacts with sodium ethoxide in ethanol, producing a red color, which is discharged by weak acids such as phenols. Evidence from kinetics[76] and from nmr spectroscopy[77] indicates that these reactions are proton transfers.

$$NO_2C_6H_4CH_2CN \underset{HA}{\overset{OEt^-}{\rightleftharpoons}} [NO_2C_6H_4CHCN]^-$$

The rates of reaction of $NO_2C_6H_4CH_2CN$ and $NO_2C_6H_4CD_2CN$ with ethoxide ion have been measured[78] over a range of temperatures from $-60°$ downwards; the reactions were rather fast and the rates were measured in a stopped-flow apparatus (see ref 89). The Arrhenius plots are slightly complicated at the higher temperatures, apparently because of a preliminary complex formation, but over a 30°-range they are linear.

The ratio k^H/k^D rises rapidly as the temperature falls, from 10 at $-60°$ to 28 at $-90°$. (This must include a secondary isotope effect, but the correction for this is unlikely to exceed a few per cent.) The difference in activation energies $E^D_{obsd} - E^H_{obsd}$ is 1.85 ± 0.2 kcal mole^{-1}, and the ratio A^D_{obsd}/A^H_{obsd} is about 5. These values suggest that there is an appreciable tunneling correction. The equations for a symmetrical parabolic barrier give 1.63 Å for the barrier width, comparable with that found for the reaction of ethoxide ion with 1-bromo-2-phenylpropane in ethanol. This is confirmed by an investigation[79] of the proton-transfer reaction at temperatures down to 124°, when deviations from a linear Arrhenius plot are observed, as described later in section IV.A.4.

g. The Deuterium Isotope Effect in the Reaction of Allylmercuric Iodide with Hydrogen Ion in Water

Allylmercuric iodide reacts with aqueous acid in the presence of traces of iodide ion; the rate is independent of the iodide concentration, and the rate-determining step appears to be the proton transfer from solvated H$^+$ to the γ-carbon.

$$CH_2{=}CHCH_2HgI + H^+ + I^- \longrightarrow CH_3CH{=}CH_2 + HgI_2$$

The primary isotope effect has been studied by a competition method.[80] From the value of A^D_{obsd}/A^H_{obsd}, the barrier width calculated for a symmetrical parabolic barrier is about 1.3 Å. This is quite similar to the values found for other reactions involving the transition $C\cdots HO \rightarrow CH\cdots O$ in water, although the neighboring group is quite different.

h. The Deuterium Isotope Effect in the Reaction of *t*-Butoxide with Bromobifluorenyl in *t*-Butyl Alcohol

When 9-bromo-9,9′-bifluorenyl is treated with potassium *t*-butoxide in *t*-butyl alcohol, abstraction of HBr occurs at a rate which appears to be controlled by a proton transfer.[81] The ratio k^H/k^D is about 8; measurements at two temperatures (30 and 40°) give $E^D_{obsd} - E^H_{obsd} \simeq 2.6$ kcal mole^{-1} and $A^D_{obsd}/A^H_{obsd} \simeq 10$. These values suggest that tunneling is important, but measurements over a wider range of temperatures are desirable.

i. The Deuterium Isotope Effect in the Reaction of Leuco Crystal Violet with Chloranil in Acetonitrile

We turn now to an example of hydride-ion transfer. This has become of special interest in view of Lewis' suggestion that repulsion will favor a large tunneling correction by producing a steep potential-energy barrier; the hydride ion H$^-$ with its two electrons will encounter repulsion forces which are absent in the transfer of H$^+$ which has no electrons.[82,83] The reaction on which the most complete results are available is the oxidation of 4,4′,4′′-tris(dimethylamino)-triphenylmethane (leuco crystal violet) by tetrachloropara-benzoquinone (chloranil).[8,84]

The isotope effect was studied in acetonitrile, in which solvent the kinetics are uncomplicated.[8] The deuterium isotope effect was measured from 10 to 35°. At 25°, k^H/k^D has the fairly large value of 11.7; the temperature coefficient gives $E^D_{obsd} - E^H_{obsd} = 3.36$ kcal mole^{-1} and $A^D_{obsd}/A^H_{obsd} = 24 \pm 10$. These are large effects, comparable with those shown by the reaction of 2-carbethoxycyclopentanone with fluoride ion (section IV.A.3.a), and clearly indicate tunneling. The value of the barrier width computed for a symmetrical parabolic barrier is 0.97 Å. Moreover the tritium isotope effect at 35.5° gives $k^H/k^T = 20.4 \pm 1.3$, whereas the Swain equation (with $r = 1.442$) predicts from the deuterium isotope effect the value 27.3; the deviation is significant and is attributable to the neglect of tunneling in the derivation of the Swain equation.

j. The Oxidation of 1-Phenyl-2,2,2-trifluoroethanol by Alkaline Permanganate in Water

The stoichiometric equation for this reaction is

$$PhCHOHCF_3 + 2MnO_4^- + 2OH^- \longrightarrow PhCOCF_3 + 2MnO_4^{2-} + 2H_2O$$

The mechanism is not entirely clear, but the rate-determining step is probably either a hydride-ion transfer from $(PhCHOCF_3)^-$ to MnO_4^-, as suggested by Stewart and van den Linden,[85–87] or a proton transfer to water with a simultaneous electron transfer to MnO_4^- as favored by Hulett.[88] The isotope

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(77) M. R. Crampton, *ibid.*, *B*, 85 (1967).

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(86) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, Chapter V.

(87) W. A. Waters, "Mechanisms of Oxidation of Organic Compounds," Methuen, London, 1964, pp 116–118.

(88) J. R. Hulett, *Discussions Faraday Soc.*, **39**, 58 (1965).

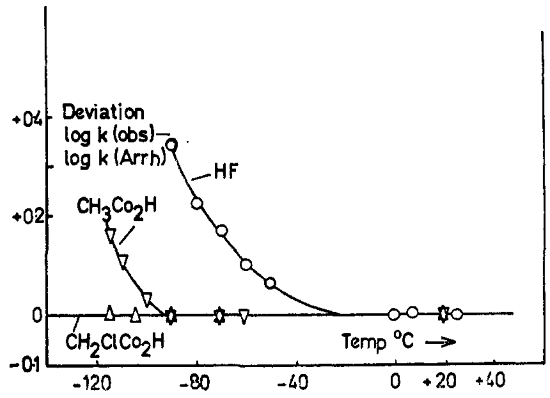

Figure 11. Deviations from linear Arrhenius plots for reactions of trinitrobenzyl anion with undissociated acids: O, HF; ∇, CH_3CO_2H; Δ, CH_2ClCO_2H. Rates were measured with a stopped-flow apparatus for HF at 25, 7, and 0°, for CH_3CO_2H at 20°, and for CH_2ClCO_2H at 20°; otherwise by conventional spectrophotometry

Table IV

Deviations from Linear Arrhenius Plots for Reactions of the Trinitrobenzyl Anion with Undissociated Acids[a]

Temp, °C	*Log k (obsd) − log k (Arrh)* *HF*	*CH_3CO_2H*	*CH_2ClCO_2H*
25	0.000 ± 0.012		
20		−0.006 ± 0.035	0.000 ± 0.013
7	+0.004 ± 0.020		
0	−0.001 ± 0.015		
−50	+0.064 ± 0.024	+0.012 ± 0.012	
−60	+0.016 ± 0.038	+0.000 ± 0.004	
−70	+0.170 ± 0.026	−0.002 ± 0.007	+0.001 ± 0.014
−80	+0.225 ± 0.020	...	
−90	+0.345 ± 0.059	−0.005 ± 0.010	+0.004 ± 0.008
−100		+0.033 ± 0.010	
−105		...	−0.002 ± 0.006
−110		+0.109 ± 0.006	
−114		+0.161 ± 0.005	+0.052 ± 0.011

[a] Solvent: ethanol + 1% toluene by volume. Experimental uncertainties are standard deviations by least squares. Some temperatures are slightly rounded.

effect[85] is considerable, though not outside the classical limit; at pH 13, k^H/k^D at 25° is 16. The temperature coefficient is not known with any precision; rates at pH 13 were measured at three temperatures (12.65, 25, and 38.0°) but the Arrhenius plots are not linear. Taking the least-squares best lines, Hulett[87] found $E^D_{obsd} - E^H_{obsd} = 2.3$ kcal mole^{-1} and $A^D_{obsd}/A^H_{obsd} = 3.0$. On fitting Bell's equations for a symmetrical parabolic barrier to these results, he found $E^H = 11.42$ kcal mole^{-1}, $E^D = 12.73$ kcal mole^{-1}, and $2a = 1.106$ Å. This barrier width is comparable with that for the reaction of 2-nitropropane with 2,6-substituted pyridines, which is the smallest yet reported and has been interpreted in terms of a steep-sided potential-energy curve due to steric repulsion. If the present reaction does indeed involve the transfer of a H^- ion, which unlike H^+ will be subject to repulsion, its small barrier width could be given a similar interpretation. The tritium isotope[8] at 25° is $k^H/k^T = 57.1 \pm 0.24$; this is in agreement with the value (55.5) predicted by substituting the value of k^H/k^D in the Swain equation.

It may be remarked that reactions whose rate-determining steps are thought to involve proton transfer as well as H^- transfer do not show evidence for tunneling,[8] no doubt because the effective mass is too large.

4. Nonlinear Arrhenius Plots

a. Introduction

Although Arrhenius plots may deviate from linearity for other reasons besides tunneling,[89] there are cases where the alternative reasons are unlikely, and the deviations are probably due to the tunnel corrections. These investigations require rate measurements to be made over a long temperature range in which the rate constant may vary by a factor of 10^5. To measure such a range of rates may require more than one technique. In the examples to be considered, measurements at the higher temperatures were obtained by the stopped-flow method (ref 46, Chapter 3); many of them were made in an apparatus[89] that could if necessary be used down to −120°. At the lower temperatures, fast observation may not be necessary and the essential is a good cryostat.[90]

b. Reactions of the Trinitrobenzyl Anion with Undissociated Acids in Ethanol

When 2,4,6-trinitrotoluene (TNT) is treated with sodium ethoxide in ethanol, it gives a deep red solution containing the trinitrobenzyl anion $C_6H_2(NO_2)_3CH_2^-$. The reaction is reversed by weak acids, and it is possible to determine the rate constants for the undissociated acids HA. These rate constants obey the Brønsted relation,[54] indicating that the rate-determining step is a proton transfer; this is confirmed[91] by the isotope effect for the forward reaction ($k^H/k^D \simeq 12$ at −30°). The scheme is thus

$$C_6H_2(NO_2)_3CH_3 \underset{HA}{\overset{OEt^-}{\rightleftharpoons}} C_6H_2(NO_2)_3CH_2^-$$

The solvent used is ethanol, to which is added 1% of toluene by volume to keep the TNT in solution; the rate is not sensitive to the toluene content.

The acids that have been studied are hydrofluoric,[92] acetic,[93] and monochloroacetic.[93] The rate for monochloracetic acid shows only a small deviation even at −114°; that for acetic shows appreciable deviation below −90°, rising to 45% at −114°; and that for hyrofluoric shows deviations below −20°, rising to over 100% at −90°. These deviations are illustrated in Figure 11, which shows the data collected in Table IV. The Arrhenius plot for the reaction of acetic acid is shown in Figure 12; the deviations from it, with their experimental uncertainties, are shown in Figure 13.

The barrier dimensions calculated from the deviations

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(90) E. F. Caldin and R. A. Jackson, *J. Chem. Soc.*, 2410 (1960).

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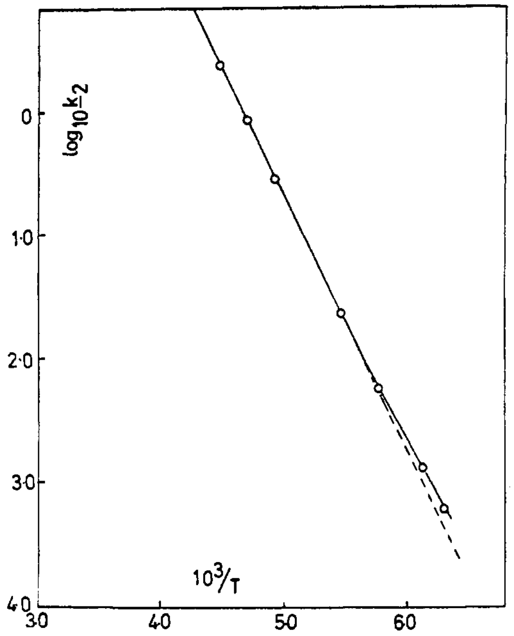

Figure 12. Arrhenius plot for the reaction between acetic acid and the trinitrobenzyl anion $[C_6H_2(NO_2)_3CH_2]^-$ in ethanol from −50 to −114°. The straight line is the best line through the points from −50 to −90°. The standard deviations are too small to show on this scale. There is also a point for +20° which lies well on the line but is omitted so as to permit a scale large enough to show the divergence at low temperatures.

Table V

Arrhenius Activation Energies for Reactions of Trinitrobenzyl Anion with Acids, and Barrier Dimensions Calculated for a Symmetrical Parabolic Barrier[a]

	HF	*CH_3CO_2H*	*CH_2ClCO_2H*
E^H_{obsd}	11.1 ± 0.1	9.38 ± 0.03	8.23 ± 0.01
E^H	11.7	10.1	8.86
$2a$	1.48	1.66	1.66
E^H_{obsd}/E	0.95	0.93	0.93

[a] E in kcal mole^{-1}; a in Å.

with hydrofluoric[66] and acetic[93] acids, assuming symmetrical parabolic barriers, are given in Table V. For monochloroacetic acid, the deviations are too small to give independent values, but the results are in agreement with the assumptions that the values of a and E^H_{obsd}/E^H are the same as for acetic acid. Comparisons will be made later; here we will only note that the barrier width is decidedly larger than for the reactions in aqueous solution discussed above, and comparable with that for the reaction of ethoxide ion with 2-bromo-1-phenylpropane in ethanol.

Alternative explanations of these curved Arrhenius plots must be considered.[92,93] (i) A change in the over-all mechanism of reaction is unlikely. The rate laws are the same at all temperatures; the original TNT is quantitatively regenerated at the end of the reaction, and absorption spectra give no indication of any new species at low temperatures. (ii) The possibility that variations in the activation energy are attributable to changes in solvation on forming the transition complex must be considered (*cf.* above, p 145). It leads to eq 36; this cannot be fitted to the experimental data, which show much too sharp a change at low temperatures. Moreover, for acetic acid the entropy of activation (−16.5 cal deg^{-1} mole^{-1}) indicates an increase of solvent orientation on formation of the transition complex, which would lead to a $\Delta C_p^{\ddagger}$ giving a curvature of the Arrhenius plot in the wrong direction. (iii) Any interpretation based on a change in the structure of the solvent at low temperatures seems to be excluded by the fact that the deviations occur at widely different temperatures for the three acids, as shown in Figure 11. (iv) There is always the possibility that a reaction may proceed through alternative transition states, with different activation energies; one of these transition states might involve only the two reactant molecules, the other a bridging solvent molecule as well.[94] This hypothesis would be difficult to test, and has not been disproved. The interpretation of the curved Arrhenius plots in terms of tunneling, however, is self-consistent and not unreasonable. Unfortunately it is impossible to determine the deuterium isotope effect for these reactions in the same solvent, because of rapid exchange between the acid and ethanol. Such a check is possible for the reaction to be mentioned next.

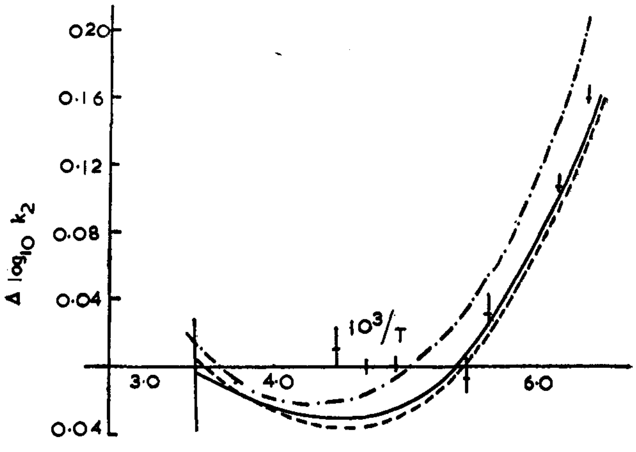

Figure 13. Deviations from linear Arrhenius plot, corresponding to Figure 12. The short vertical lines represent the experimental values of [log k_2(obsd) − log k_2(Arrh)], with their standard deviations. The curves are calculated values of [log k_2 − log k_2(Arrh)] for various assumed values of the barrier height (E^H) and width ($2a$), for a symmetrical parabolic barrier. Full curve, $E^H = 10.05$ kcal mole^{-1}, $a = 0.84$ Å; - - -, $E^H = 10.10$ kcal mole^{-1}, $a = 0.83$ Å; -·-·-, $E^H = 10.10$ kcal mole^{-1}, $a = 0.81$ Å.

c. The Reaction of Ethoxide Ion with 4-Nitrobenzyl Cyanide in Ethanol–Ether

It has already been mentioned (p 150) that the isotope effect in this reaction indicates a considerable tunneling correction for the proton-transfer rate. The reaction also exhibits deviations from a linear Arrhenius plot at low temperatures.[79] The Arrhenius plot is linear within experimental error from −70 to −100°, but at −120° there is an appreciable deviation and at −124° it amounts to 100% in the rate. (Ethanol–ether (20/80 v/v) had to be used as solvent rather than pure ethanol in order to decrease the freezing point and increase the fluidity at low temperatures.)

The curvature of the plot at the lowest temperature is ex-

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(94) E. Grunwald and M. Cocivera, *Discussions Faraday Soc.*, 39, 105 (1965).

ceptionally sharp. Consequently the theoretical equations for a parabolic barrier cannot be fitted to the experimental results for this reaction quite so well as for the reactions of the trinitrobenzyl anion. The values found for the barrier dimensions are nevertheless equally well defined and agree well with those derived from the isotope effect.[78] The values are summarized in Table VI.

Table VI

Comparison of Barrier Dimensions Calculated from the Isotope Effect and for the Arrhenius Plot for the Reaction of Ethoxide Ion with 4-Nitrobenzyl Cyanide in Ethanol–Ether

	Isotope effect	*Arrhenius plot*
E^H, kcal mole^{-1}	10.3 ± 0.1	10.7 ± 0.1
$2a$, Å	$1.63_2 \pm 0.01$	$1.62_2 \pm 0.01$

The agreement between the two independent values of the barrier width $2a$ is satisfactory. This agreement supports the interpretation of the nonlinear Arrhenius plot in terms of tunneling. This reaction appears to be the first for which the two methods of detecting tunneling have been applied to the same reaction in the same medium.

B. GENERAL DISCUSSION OF EXPERIMENTAL WORK ON TUNNELING IN SOLUTION

1. *Comparison of Barrier Dimensions*

Table VII shows most of the reliable data so far available on the dimensions of the energy barriers in proton-transfer reactions. They have all been obtained by applying Bell's equations,[19] usually in the first-term approximation, for tunneling through one-dimensional symmetrical parabolic barriers. In general the fit of the equations to the experimental data is such that the value of the barrier height can be given to ±0.1 kcal mole^{-1}, and the width $2a$ to ±0.01 Å. The reactions so far studied involve only small tunneling corrections, giving rise to values of E^H_{obsd}/E^H between 0.75 and 1. The curvature at the top of the barrier is therefore the quantity that determines the tunneling correction; it may be expressed as the frequency ν_t (eq 24), and values of this are given in Table VII.

The values of the barrier dimensions are subject to the various uncertainties already mentioned (p 146). The effective barrier width is probably larger than $2a$, but it is impossible to give a precise expression. The barrier height will be affected if there are appreciable contributions to the energy of activation from solvation changes, or if the reaction involves changes of configuration consequent upon electronic reorganization. The calculations refer to a symmetrical energy barrier for which $\Delta H° = 0$; some of the values might well be changed if the enthalpy change in reaction were taken into account.

It seems worthwhile, in spite of these uncertainties, to attempt some comparisons between the reactions 1–14 in Table VII and to hazard some tentative generalizations on the factors that favor tunneling. Valid comparisons might be expected particularly for closely related pairs of reactions such as 2 and 3, which differ only in the base, involving the transfers CH···O and CH···F respectively; or between 9 and 10, which differ only in the acid, involving the transfers

Table VII

Tunneling in H-Transfer Reactions. Computed Dimensions of Energy Barriers[a]

Reaction[b]	*Ref*	*Type*	*Solvent*	*Method*	$2a$	E^H	E^D	E^T	c_t	ν_t	E^H_{obsd}/E^H
1. 2-CCP + D_2O	60	CH···O	D_2O	H, D	1.26	13.1_6	13.5_5	...	66.1	878	0.90
2. 2-CCP + $CH_2ClCO_2^-$	60	CH···O	D_2O	H, D	1.17	12.5_3	12.9_5	...	73.5	924	0.88
3. 2-CCP + F^-	60	CH···F	D_2O	H, D	1.17	18.0_1	18.0_7	...	104	1106	0.81
4. Acetone + OH^-	65	CH···O	H_2O	H, D	1.26[c]	13.6	14.7	...	68.5	894	0.91
5. *p*-MOAP + OH^-	64	CH···O	H_2O	H, T	1.22[c]	15.9	...	17.1	86.0	1001	0.87
6. *o*-MAP + OH^-	69	CH···O	H_2O	H, T	1.27[c]	14.1	...	15.5	69.9	908	0.84
7. Me_2NO_2CH + B	8, 71	CH···O	*t*-BuOH–H_2O	H, D	1.14	16.3	17.6	...	100	965	0.88
8. $CH_2BrCMePhH$ + OEt^-	75	CH···O	EtOH	H, D, T	1.59	22.1	23.0	23.4	69.9	908	0.95
9. TNT anion + HOAc	93	C···HO	EtOH	Arrh	1.66	10.1	...	...	29.3	585	0.93
10. TNT anion + HF	92	C···HF	EtOH	Arrh	1.48[c]	11.7	...	...	42.6	717	0.95
11. 4-NBC + OEt^-	79	CH···O	EtOH–Et_2O	Arrh	1.62[c]	10.7	...	...	32.5	616	0.86
12. 4-NBC + OEt^-	78	CH···O	EtOH–Et_2O	H, D	1.63	10.3	11.3	...	30.9	600	0.89
13. $CH_2{=}CHCH_2HgI$ + H^+	80	C···HO	H_2O	H, D	1.3	...	...	...	...	...	...
14. $(p\text{-}Me_2NC_6H_4)_3CH$ + CA	8	CH···O	MeCN	H, D	0.97	...	...	...	51.6	1150	0.72

[a] Calculated values from Bell's equations for symmetrical parabolic barriers. E^H_{obsd} = Arrhenius activation energy for H transfer, derived from linear part of Arrhenius plot, in kcal mole^{-1}. E^H, E^D, E^T = heights calculated for energy barriers for H, D, and T transfer, in kcal mole^{-1}. $2a$ = width of parabolic energy barrier at base, in Å. c_t = curvature of parabola at apex $2E^H/a^2$ in kcal mole^{-1} Å^{-2}. ν_t = frequency corresponding to barrier dimensions = $c^{1/2}/2\pi m^{1/2}$ (see text). [b] 2-CCP = 2-carbethoxycyclopentanone. *p*-MOAP = *p*-methoxyacetophenone. *o*-MAP = *o*-methylacetophenone. B = 2,4,6-collidine. TNT = 2,4,6-trinitrotoluene. 4-NBC = 4-nitrobenzyl cyanide. CA = chloranil. [c] Recalculated; ref 66.

C···HO and C···HF. The factors that might be expected to be relevant are (i) the atoms between which the proton is transferred; (ii) the charges on these atoms; (iii) the electronic properties of the groups attached to these atoms; (iv) steric and repulsion factors; and (v) the medium.

When we examine the data, two major factors stand out: the effects of steric hindrance, or more generally repulsion energy, and that of the solvent. Other influences appear to be comparatively small.

a. The Atoms between Which the Proton is Transferred

We might have expected, on the simple potential-energy picture of proton transfer, that these atoms would be the most important influence on the barrier width, since their repulsions will determine the minimum van der Waals distance of approach in a nonreactive collision (AH···B) and the bond lengths A–H and $H–B^+$ will then fix the distance that the proton has to travel in the reaction. Examination of Table VII shows, however, that other factors are also involved. For reactions of the type CH···O and CH···F, the distances so calculated are nearly the same (1.35 and 1.34 Å), but the calculated curvatures are seen to be larger for the CH···F reactions (compare reaction 2 with 3, or 9 with 10). The curvature varies considerably for a given type of reaction; moreover, for reactions of type CH···O it varies more than threefold, and more than twofold for reactions of type CH···F or C···HF.

b. The Charges on the Atoms

A comparison of reactions 1 and 2 may indicate the effect of the charge on the oxygen atom when the other conditions are as similar as possible. The curvature is slightly larger for reaction 2 than for reaction 1, possibly because of the extra attraction of the negatively charged oxygen of the anion for the proton.

c. The Electronic Properties of the Neighboring Groups

The groups attached to the atoms between which the proton is transferred might affect the barrier width in several ways. As donors or acceptors of electrons, they will decrease or increase the strength of any hydrogen bond that may be formed before the proton transfer occurs, and will also affect the repulsion between the two reactants; and if conjugation can occur, it will alter the distribution of charge and the effective charge on the carbon atom, and so affect the repulsive forces. However, if we compare the pair of reactions 2 and 9 (type CHO) with the related pair 3 and 10 (type CHF), the predicted effects are the reverse of those observed; in reactions 9 and 10 the carbon atom is conjugated with $C_6H_2CH_2(NO_2)_3^-$, whereas in reactions 2 and 3 it is conjugated with C═O whose effect should be weaker, yet the curvature is markedly larger (by a factor >2) for reactions 2 and 3. It is clear that these factors are not the dominant ones.

d. Steric and Repulsion Factors

We have noticed in section IV.A that in the reactions of 2-nitropropane the largest effects occur with 2,6-substituted pyridines, such as reaction 7 in Table VII, where steric hindrance implies a considerable repulsion contribution to the potential energy, and hence a steep-sided barrier with a high curvature, which will favor tunneling. The value of the barrier width is the smallest and the curvature the largest yet reported. Another considerable effect is seen in reaction 14, where the rate-determining step is the transfer of H^-, again involving unusual repulsion forces. Both experimentally and theoretically this repulsion factor appears to be important. It is not the whole story; examination of models does not suggest that steric hindrance will be much greater for reactions 9 and 10 than for 2 and 3, as would follow from the values of the curvature if it were the only relevant factor. This brings us to the other main influence, that of the solvent.

e. The Solvent

There is a clear-cut difference between the values of the barrier width for reactions in alcoholic solutions and those in aqueous solutions; the first have high values (1.48–1.66 Å) and the second low values (1.08–1.26 Å). This difference appears also in the curvatures, except for reaction 8; for alcoholic solutions the figures are 30 to 43, as against 66 to 104 for aqueous solutions. The high and low values do not correlate with the type of reaction (CHO or CHF). The number of reactions is small, so the correlation with solvent may be fortuitous, but it can hardly be ignored. A possible reason[92] for it is that solvating ethanol molecules are more bulky than water molecules, so that the effective barrier width is larger. Another possibility is that solvent water molecules participate in the reaction, as has been shown to occur in some proton transfers,[94,95] whereas this is less likely for alcohol molecules.

The difference between the barrier widths for C···HO and C···HF reactions in ethanol (9 and 10) may be due to the hydrogen-bonding properties of fluorine. There is no direct evidence for hydrogen bonds involving carbon and fluorine, but HF is known to form strong hydrogen bonds, and CH–O and CH–N hydrogen bonds are well established in chloroform solutions and HCN, respectively.[96] Hydrogen bonding of CH to the anions may thus occur in ethanolic solution, and more strongly with fluorine than with oxygen, with a consequent shortening of the CH–F distance relative to the CH–O distance. In water, with its higher dielectric constant, this hydrogen bonding would be expected to be weaker and its effect on the barrier width less marked.

2. *Isotope Effects on the Heights of Energy Barriers and the Symmetry of Transition Complexes*

An interesting example of the use of the information on barrier heights which we owe to investigations on tunneling concerns the correlation of isotope effects with the symmetry of transition states. The following is taken mostly from a recent paper.[66]

The values found for E^H, E^D, and E^T (Table VII) represent the heights of the energy barriers, taking account of zero-point energies in the initial and transition states. If the isotope effect arose entirely from differences in the initial states of the bonds broken, we should expect $(E^D - E^H)$ to be equal to the difference of the zero-point energies (zpe) in the initial states, ΔE_{zpe}^{init}, which is 1.1 to 1.2 kcal $mole^{-1}$ for a C–H bond. Inspection of Table VII shows that this is not the case for several of the reactions. This implies that for these reac-

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(95) W. J. Albery, *Progr. Reaction Kinetics*, 4, 353 (1967).

(96) G. Pimentel and A. L. McClellan, "The Hydrogen Bond," Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 6.

Table VIII

Barrier Heights and p*K* Differences for the Ionization of Some C–H Bonds[a]

Reaction[b]						
Acid (SH)	*Base (B)*	*Medium*	*pK(SH)*	*pK(BH)*	*ΔpK′*	$(E^D - E^H)$
2-CCP	D_2O	D_2O	10.52[c]	−1.70	11.74	0.2_8
2-CCP	$CH_2ClCO_2^-$	D_2O	10.52[c]	3.20	6.84	0.4_2
2-CCP	F^-	D_2O	10.52[c]	3.62	6.42	0.0_6
Acetone	OH^-	H_2O	19.00	15.74	3.74	1.1
p-MOAP	OH^-	H_2O	20.1	15.74	4.5_4	1.0[d]
o-MAP	OH^-	H_2O	19.9	15.74	4.3_4	0.9[d]
2-Nitropropane	B	*t*-BuOH–H_2O	7.74	7.43	0.31	1.2
4-NBC	OEt^-	EtOH–Et_2O	14.0	19.1	−5.4	1.0

[a] E^D and E^H in kcal $mole^{-1}$. [b] See Table VII for abbreviations. [c] Solvent isotope effect neglected. [d] Values of $(E^D - E^H)$ estimated from $(E^T - E^H)$.

tions there is a difference between the zero-point energies in the transition states for the two isotopes, $\Delta E_{zpe}{}^{\ddagger}$, which partly cancels $\Delta E_{zpe}{}^{init}$ according to the equation

$$(E^D - E^H) = \Delta E_{zpe}{}^{init} - \Delta E_{zpe}{}^{\ddagger}$$

It has been shown by Bell and Goodall[97] that, for a series of similar proton-transfer reactions in water, the isotope effect on the rate (k^H/k^D) is correlated with the p*K* of the reaction and passes through a maximum when the p*K* is zero. This corresponds to the theoretical treatment of Westheimer,[98] which predicts that the isotope effect will be a maximum when the transition state is symmetrical; there will then be no zero-point energy for the stretching vibration in the transition state, and hence a maximum value of $(E^D - E^H)$; also the free-energy change in the reaction, and so the value of Δp*K*, which is a rough measure of the departure of the transition state from symmetry, will be approximately zero. In Table VIII are summarized all the known values of $(E^D - E^H)$ for proton transfers involving the breaking of C–H bonds in compounds whose p*K*'s are reliably known in aqueous solution.[99] Since the value of p*K* is partly determined by statistical factors, we give the statistically corrected quantity $\Delta pK' = \Delta pK + \log (p_{SH}q_B/p_{BH}q_S)$, where *p* and *q* represent the number of equivalent protons and basic sites, respectively.[97] A plot of $(E^D - E^H)$ against Δp*K*′ is shown in Figure 14. A smooth curve can be drawn through most of the points, with a maximum around $\Delta pK' = 0$. It is noteworthy that the point representing the reaction of 2-nitropropane with 2,4,6-trimethylpyridine lies quite well on the curve, whereas the corresponding point for $\log (k^H/k^D)$ was anomalous in lying well off Bell and Goodall's plot; this can be understood, since among the reactions considered by them it was the only one to exhibit tunneling, whose effects are removed when we consider the true barrier heights, as in Figure 14.

For several reactions the value of $E^D - E^H$ is about 1.1 kcal $mole^{-1}$, which is close to the theoretical maximum calculated on the assumption that the stretching frequency of the C–H or C–D bond in the initial state is the important factor. This suggests that in these reactions the zero-point energies of the bending vibrations in the transition state approximately cancel those of the bending vibration involving H or D in the initial state. For the other reactions, the correlation shown in Figure 14 suggests that these zero-point energies (reflected in the values of E^D and E^H) increase with the departure of the transition state from symmetry (represented by Δp*K*′), as would be expected from the theoretical picture.

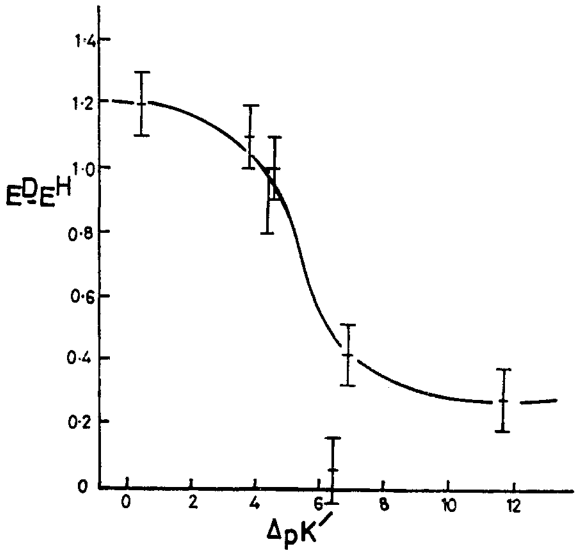

Figure 14. Plot of $E^D - E^H$, calculated for various reactions on the assumption of a symmetrical parabolic barrier, against Δp*K*′.

One point lies well off the curve; the reaction concerned is the fluoride-catalyzed bromination of 2-carbethoxycyclopentanone. The deviation could be attributed to an unusually large value of $\Delta E_{zpe}{}^{\ddagger}$, which could arise either because the C···H···F transition state is more unsymmetrical than would be expected from the p*K* of the reaction, or because the transition state has a high bending vibration frequency as well as a stretching frequency, or for both reasons. Both effects may be related to the strong hydrogen bonds formed by fluorine.[60,96]

3. Very Fast Proton-Transfer Reactions

In all the reactions so far considered, the proton is transferred to or from a carbon atom. Such reactions proceed at moderate rates, whereas proton-transfer reactions involving

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[97] R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, A294, 273 (1966).

[98] F. H. Westheimer, *Chem. Rev.*, 61, 265 (1961).

[99] The table is taken from ref 66, with the exception of a new experimental value for the p*K* of *o*-methylacetophenone, for which I am indebted to a personal communication from Dr. J. R. Jones.

only oxygen or nitrogen acids (*e.g.*, ROH or R_3NH^+) are very fast; their rates approach the diffusion-controlled value, corresponding to reaction at every encounter. There is good evidence that in water such proton transfers take place through a hydrogen-bonded system, such as $OH\cdots O$. The O atoms are then much closer than in a van der Waals encounter, and the potential-energy barrier is therefore much narrower than for nonhydrogen-bonding systems such as carbon acids; it could be as thin as 0.5 Å. The height of the barrier is not known with any accuracy; it will be reduced by the hydrogen bonding, but probably not to zero. (If the reactants are linked by one or more water molecules, the barrier height may be reduced because of the cooperative movement of protons along the hydrogen-bonded chain; but there are instances where it is known that no water molecules intervene, either through nmr investigations such as those of Grunwald on aqueous amines,[100] or because the reaction occurs in a nonhydrogen-bonding solvent such as chlorobenzene,[101] and here the barriers are probably appreciable.) The very high rate would then be unexpected, unless it is due to tunneling, as was suggested by Eigen.[102] The tunneling correction for so thin a barrier can be large; calculations by Grunwald[103] suggest that the rate could reach the diffusion-controlled value even if the height of the energy barrier were around 10 kcal mole^{-1}. Confirmation of this suggestion must await firmer estimates of the heights of these barriers.

V. Conclusion

Quantum-mechanical tunneling in H^+-transfer reactions, which for 20 years eluded experimentalists, now appears to be past the stage of discovery. It would be difficult to think of an alternative explanation that would cover all the evidence presented above, such as the high values of A^D/A^H and of A_{i}^T/A^H, or the agreement of the deductions from H transfer and T transfer where these have both been studied, or the agreement in the one available instance between the barrier dimensions calculated from isotope effects and from the Arrhenius plot. The tunnel effect is by now the likeliest interpretation of the evidence on several reactions. It remains true that such reactions appear to be exceptional and that in most proton-transfer reactions the tunneling corrections can probably be ignored.

The next phase should be that of systematic study. This presupposes some hypotheses about which systems are likely to be worth investigating. At present the suppositions that seem plausible are that tunneling is favored by a high contribution to the activation energy from repulsion, whether in sterically hindered reactions or in hydride-ion transfer, since this produces a step barrier; by small barrier widths as in H transfers along hydrogen bonds; by a symmetrical energy barrier, corresponding to a low enthalpy of reaction; and by some effect, not yet understood, of water as solvent. Much more experimental work is needed, especially on related series of reactions and on solvent effects. Computations from Bell's theoretical equations have usually been confined to the first approximation; they should be carried to a higher accuracy and should also be extended to take account of the enthalpies of reaction; experimental work to determine these enthalpies is needed as well.

The object of work in this field, apart from confirming the importance of tunneling corrections in such reactions, is to enlarge our knowledge of the shapes and dimensions of energy barriers, and so improve our picture of transition states. We have seen (p 154) that the correction of the observed energy of activation to the true barrier height by means of the tunneling correction can lead to interesting results. The barrier width is a more elusive quantity, partly because of our ignorance of barrier shapes; but the discussion above shows that a start has been made, and we may expect that as results on more systems become available a clearer picture of the entire energy profile will emerge. There are very few sources of information on barrier dimensions, and the contribution of work on tunneling seems likely to be of importance.

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(101) E. F. Caldin and J. E. Crooks, *J. Chem. Soc.*, 959 (1967).

(102) M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, 3, 1 (1964).

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