ISOTOPE EFFECTS AND QUANTUM-MECHANICAL TUNNELING

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NOTICE

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Introduction

The phenomenon of quantum-mechanical tunneling is not observable in the macroscopic world which we experience directly. Suppose that a ball is rolled along the ground towards a small ridge. If its kinetic energy is greater than the potential energy of the ball at the top of the ridge it will surmount the barrier; if the kinetic energy is less than this, the ball will not get over the hill.

However, a moving particle of atomic or electronic mass does not obey Newtonian mechanics. Instead, it behaves as a wave packet with a wavelength given by the de Broglie expression

$$\lambda = h/mv, \quad (1)$$

where h is Planck's constant, m is the mass of the particle, and v its velocity. For purposes of calibration, it is convenient to remember that a hydrogen atom, moving with thermal velocity at 300°K, has a wavelength of about 1 Å (0.1 nm).

When such a particle encounters a barrier, represented by an increase in potential energy, it does not behave like a macroscopic particle. Instead, there is a finite probability of "leakage" or "tunneling" through the barrier even if the kinetic energy is less than the potential energy at the barrier summit; conversely, there is a finite probability of reflection even if the kinetic energy is greater than this. The extent of tunneling, the transmission probability κ , is defined by $\kappa = (A_t/A_i)^2$, where A_i and A_t are the wave function amplitudes for the incident and transmitted waves (Fig. 1).

As one would expect, κ depends on the mass of the particle, its velocity, and the shape and height of the barrier. Two convenient parameters are

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$$\alpha = 2\pi V^*/h\nu^* \quad \text{and} \quad \epsilon = E/V^*, \quad (2)$$

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where V^* is the barrier height and ν^* is a "vibrational frequency" defined by

$$\nu^* = (2\pi)^{-1} \{-\mu^{-1} [d^2V(x)/dx^2]\}^{1/2}, \quad (3)$$

where μ is the reduced mass appropriate to motion in the x direction. For a particular form of the potential barrier, $V(x)$, known as the Eckart barrier (see below), the dependence of κ on ϵ and α is shown in Fig. 2. The classical limit is simply a step function at $\epsilon = 1$, i.e. when the kinetic energy of the particle is equal to the potential energy at the barrier summit. Large values of α , corresponding to high, or nearly flat, barriers lead to a similar form of κ . Low values of α , on the other hand, lead to finite values of κ with ϵ much less than unity, and to values of κ less than unity even when E is greater than V^* .

The physical significance of quantum-mechanical tunneling was recognized very early in the development of wave mechanics, and there are many examples of physical phenomena in which tunneling is important. Here is a very incomplete list of examples, chosen principally on the basis of historical interest:

1. The cold emission of electrons from a metal cathode at a high negative voltage (1).
2. The emission of α -particles from an atomic nucleus (2,3).
3. The effect of the double minimum in the potential energy for NH_3 on vibrational energy levels (4).
4. The possibility of tunneling in a chemical reaction involving motion of a proton or a hydrogen atom, which seems to have been first recognized by R. P. Bell (5).
5. The tunnel diode, a semiconductor device of considerable practical importance. The discovery of this by L. Esaki in 1956-58 (6) led to his sharing in the 1973 Nobel prize for physics (7). In fact, it is interesting to note that the other two recipients of the Nobel prize in physics for that year, B. D. Josephson and I. Giaever, were also honored for discoveries involving tunneling in solids (8,9). The Nobel prize awards should, in themselves, provide ample proof of the reality and the practical significance of tunneling!

Tunneling in Chemical Reactions

Now that it has been made evident that tunneling is predicted by quantum mechanics, and that there are a number of physical manifestations of it, what about the particular area of chemical reactions?

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The potential energy of interaction for the reactants in a hypothetical reaction such as

can be represented by a contour map (Fig. 3). Along the reaction path, the potential energy has the form of a one-dimensional barrier, similar to that in Fig. 1. If the mass of the atom being transferred (B in this example) is sufficiently small, and if the barrier has suitable dimensions, tunneling may become important. I am deliberately evading here some subtle questions, such as:

1. What is the precise reaction path that should be used to obtain the one-dimensional potential?

2. Is it correct to treat the problem as one-dimensional, when the potential energy is a function of two dimensions?

These and related questions have been discussed in detail by others (10,11).

For a one-dimensional barrier of arbitrary shape, numerical methods can be used to calculate the transmission probability κ (12). Before the availability of large computers, this problem was often circumvented by approximating the barrier with an Eckart function (13). The symmetric form of this, which I shall use later, is

$$V(x) = V^* / \cosh^2[(2\mu V^*)^{1/2} \pi v^* x] \quad (4)$$

This potential has the great advantage of leading to analytical solutions of the resulting Schrödinger equation, so that much less computational effort is required to calculate κ than is required for an arbitrary barrier shape. It is ideally suited for testing the qualitative effects of changing properties of the barrier. With an Eckart barrier, the transmission probability for a particle with energy E is found to be

$$\kappa(E) = [\cosh(2\alpha e^{1/2}) - 1] / [\cosh(2\alpha e^{1/2}) + \delta] \quad (5)$$

where $\delta = \cosh(4\alpha^2 - \pi^2)^{1/2}$ ($\alpha > \pi/2$)

or $\delta = \cos |4\alpha^2 - \pi^2|^{1/2}$ ($\alpha < \pi/2$),

and the other quantities have already been defined.

In a chemical reaction system at thermal equilibrium, the Boltzmann distribution of molecular energies must be taken into account in obtaining the average transmission probability. The tunneling factor is usually defined as the ratio of this averaged transmission probability to that obtained with the classical values

$$\kappa(E) = 0, \quad E < V^*; \quad \kappa(E) = 1, \quad E \geq V^* .$$

That is,

$$\Gamma^*(T) = \frac{\int_0^{\infty} \kappa(E) \exp(-E/RT) dE}{\int_{V^*}^{\infty} \exp(-E/RT) dE} \quad (6)$$

or

$$\Gamma^*(T) = \exp(V^*/RT) \int_0^{\infty} \kappa(E) \exp(-E/RT) d(E/RT) \quad (7)$$

This expression must be numerically integrated over the appropriate energy range.

Tunneling and Kinetic Isotope Effects

The Magnitude of Primary Hydrogen Isotope Effects. As Eq.(1) illustrates, the wavelength associated with a moving particle is inversely proportional to the mass. In a comparison of two isotopic species in a chemical reaction, this mass dependence leads to different values of v^* and α . Since α is larger (v^* smaller) for the heavier species, the values of $\kappa(E)$ are closer to the classical values, and this shows up in $\Gamma^*(T)$. Since relative differences in mass are greatest for the isotopes of hydrogen, one might expect important differences in the tunneling corrections for reactions involving the motion of H, D, or T atoms or ions. In fact, almost since the discovery of deuterium, such reactions have been studied in an attempt to find evidence for tunneling in a chemical reaction (14).

To find evidence for tunneling, one must first account for kinetic isotope effects that do not depend on tunneling. The most direct method of doing this is by means of activated complex theory, which leads to a formulation of the rate constant in terms of partition functions of the reactants and the activated complex. Arguments concerning the validity of activated complex theory are easy to provoke and difficult to settle, and I shall not consider this question here. It can then be shown (15,16) that the ratio of rate constants for two isotopic forms of the same reactant (AX_1 and AX_2) is given by

$$\frac{k_1}{k_2} = \frac{v_1^* \Gamma_1^*}{v_2^* \Gamma_2^*} \frac{\prod_{i=1}^{3r-7} \Gamma_i(A\bar{X}_1^{\ddagger})}{\prod_{i=1}^{3r-7} \Gamma_i(A\bar{X}_2^{\ddagger})} \frac{\prod_{j=1}^{3r-6} \Gamma_j(A\bar{X}_2)}{\prod_{j=1}^{3r-6} \Gamma_j(A\bar{X}_1)} \quad (8)$$

Here $\Gamma_1 = u_1 e^{-u_1/2} / (1 - e^{-u_1})$, $u_1 = h\nu_1/kT$, and $3r-6$ ($3r-7$) is the number of real vibrations in the reactant (activated complex).

Given the details of the relevant potential energy surface, or some empirical scheme for predicting the force constants needed to calculate the vibrational frequencies upon which the Γ_1 's depend, one can evaluate Eq. (8) with or without the tunneling contribution Γ_1^*/Γ_2^* . A comparison with experiment should then reveal whether the tunneling correction is indeed important.

A good example of this approach is provided by the gas-phase reaction systems

which have been examined in detail by H. S. Johnston and coworkers (17,18). A comparison of experimental isotope effects and those calculated with and without tunneling is given in Fig. 4; evidently the calculations which include tunneling are in better agreement with experiment.

This approach depends for its validity on the accuracy with which Eq. (8) can be evaluated. As potential energy surfaces for larger and larger reaction systems become available, the confidence with which one can utilize this method will increase; obviously it is only as good as the force constants that go into Eq. (8). However, in some cases even the magnitude of the experimental isotope effect is so large that it seems difficult to explain without a contribution from the tunneling correction. For example, the isotopic rate constant ratio k_H/k_D for the proton (deuteron) transfer from 4-nitrophenylnitromethane to tetramethylguanidine has been found to be as high as 45 at 25°C (19).

Arrhenius Pre-exponential Factors in Primary Hydrogen Kinetic Isotope Effects. A second diagnostic test for tunneling in chemical reactions is based on the temperature dependence of tunneling. Returning again to Eq. (1), we see that as the momentum of a particle increases (due to increased thermal energy, for example) its wavelength decreases. This, in turn, leads to a temperature dependence of Γ^* , which approaches unity at high temperatures.

The way this has been expected to influence an isotopic rate constant ratio has been discussed frequently in the literature (14), and is illustrated in Fig. 5. Kinetic-isotope-effect data can be expressed in the form

$$k_H/k_D = A_Q(T) e^{B(T)/T} \quad (9)$$

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where both A_0 and B are written as temperature-dependent, for the sake of generality. If tunneling is unimportant, i.e., at high temperatures, this expression will behave like the Arrhenius expression for individual rate constants, with A_0 and B independent of temperature. Then a plot of $\ln(k_H/k_D)$ vs T^{-1} will be linear, or very nearly so. As the temperature is decreased and the tunneling component of the isotope effect becomes more important, $\ln(k_H/k_D)$ will curve upwards, so that $B(T)$ is larger and $A_0(T)$ is smaller than they would be without tunneling (Fig. 5). Bell (20), and more recently Schneider and Stern (21), have investigated the temperature dependence of A_0 for model reactions. The latter workers carried out calculations of k_H/k_D with Eq. (8) (without the tunneling correction), and by fitting these values to the form of Eq. (9), they obtained A_0 as a function of temperature. For several model reactions with large primary hydrogen isotope effects, they attempted to force A_0 values as low as possible by adjusting force constants of the model activated complexes. Over a temperature range of 20-1000°K, values of A_0 below 0.7 could not be attained. This answers part of the question: In the absence of tunneling, A_0 is restricted to a rather narrow range. The remaining part of the question is the converse: In the presence of tunneling, does A_0 lie outside this range?

To answer this, Stern and I (22) used the same model systems previously investigated by Schneider and Stern, but included the tunneling correction in the isotope effect. Values of v^* were those calculated in their work; barrier heights V^* were not needed in their work, and we have simply assumed values of 1, 5, 10, 20, and 30 kcal/mole for V_H^* . A symmetrical Eckart potential was used. For reasons discussed in our paper (22), two sets of calculations were made: one with $V_D^* = V_H^*$ and one with $V_D^* = V_H^* + 1$ kcal/mole. Although we examined all of the models used by Schneider and Stern, I shall discuss here only the results obtained from the model for the reactions $CF_3 + C_2H_6$ or $C_2H_5D \rightarrow CF_3H$ or $CF_3D + C_2H_5$.

First, the individual tunneling corrections, Γ_H^* and Γ_D^* , are shown in Fig. 6 as functions of T^{-1} . These are well-behaved, smooth, functions, although if V_H^* is not equal to V_D^* there is a crossover temperature below which $\Gamma_H^* < \Gamma_D^*$. This arises from the term $\exp(V^*/RT)$ in Eq. (7); thus, $\exp[(V_H^* - V_D^*)/RT]$ is more important than the integral at low temperatures. For the isotope-independent barrier, the ratio Γ_H^*/Γ_D^* is almost constant at low temperatures because the individual lines are parallel. At high temperatures, $\ln(\Gamma_H^*/\Gamma_D^*)$ approaches zero with a positive curvature, so that the complete $\ln(\Gamma_H^*/\Gamma_D^*)$ vs T^{-1} curve is sigmoid shaped. When the barrier height is isotope dependent, the shape of $\ln(\Gamma_H^*/\Gamma_D^*)$ is similar at high temperatures, but ultimately the values are decreased because of the exponential term discussed above, and the curve is almost a straight line with slope

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$(V_H^* - V_D^*)/R$. However, since this term has an exponential temperature dependence, it does not affect A_Q . The temperature dependence of $\ln A_Q$ (for tunneling alone) can be qualitatively assessed from Fig. 6 by linear extrapolation from a particular temperature region. This was done more precisely by using a least-squares fit to $\ln(\Gamma_H^*/\Gamma_D^*)$ or $\ln(k_H/k_D)$ at four temperatures, and the resulting values of A_Q for various barrier heights are plotted in Fig. 7a. The infinite-temperature limit of $\ln A_{Q,tun}$ is zero. At high temperatures, $\ln A_{Q,tun}$ will decrease to negative values with decreasing temperature. As the temperature is further decreased, $\ln A_{Q,tun}$ will go through a minimum at the temperature of the inflection point in the $\ln(\Gamma_H^*/\Gamma_D^*)$ curve, and then increase again as the temperature decreases further. At very low temperatures, $\ln A_{Q,tun}$ is approximately equal to $\ln \Gamma_H^* - \ln \Gamma_D^*$, which is a very large quantity. As mentioned above, there is not a significant difference between the cases with isotope-dependent and isotope-independent barrier heights.

When the tunneling correction is combined with the rest of the rate constant ratio, $(k_H/k_D)_{class}$, the resultant form of $\ln A_Q$ is almost identical with that for tunneling only. This is because $\ln(k_H/k_D)_{class}$ has almost exactly the Arrhenius form, with $\ln(A_{Q,class})$ virtually independent of temperature (see the curves labelled "NT" in Figs. 7a' and 7a'').

Figs. 7a' and 7a'' illustrate the following important features:

1. Regardless of the barrier height, there is a fairly small temperature region in which $\ln A_Q$ is below the limit of -0.69 predicted by Bell's model in the absence of tunneling (indicated by the lower dashed line). The extent of the excursion below this limit increases with increasing barrier height. It is in this temperature region that most experiments have been done, and earlier calculations of tunneling were made.

2. At lower temperatures, $\ln A_Q$ exceeds the upper limit of 0.35 predicted by Bell in the absence of tunneling (indicated by the upper dashed line). This is contrary to what had been expected before our calculations were made, because earlier calculations concentrated on the region to the left of the inflection point in Fig. 6.

3. The value of A_Q does not correlate simply with the extent of tunneling, which is indicated by values of $\ln \Gamma_H^*$ for $V_H^* = 10$ on the top of Fig. 7.

In our work, we also examined other model reactions, and a few other barrier shapes, with similar results.

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Thus, we conclude that experimental A_Q values can be used as quantitative indicators of quantum-mechanical tunneling only in conjunction with model calculations. Although A_Q values outside of Bell's range of $0.5\text{--}\sqrt{2}$ probably cannot be found in the absence of tunneling, A_Q values inside this range do not necessarily indicate the absence of large tunneling factors. In spite of this somewhat uncertain situation, it is interesting to see if there are experimental values of A_Q outside the "non-tunneling" range. Data from reactions in which tunneling has been invoked are given in Table I. (This does not mean that tunneling is unimportant in other reactions, but only that it has not been specifically searched for). Without critically evaluating the experimental data of Table I, I simply point out that there are several reactions in which abnormally low A_Q values have been observed.

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Relative Tritium-Deuterium Isotope Effects. Because some isotope experiments are best done with D substitution and others with T substitution, there has been for some time an interest in, and a necessity for, the correlation of the rate constant ratios k_H/k_D and k_H/k_T . This correlation may be defined as

$$\bar{\epsilon} = \frac{\ln(k_H/k_T)}{\ln(k_H/k_D)}$$

Several theoretical investigations of the allowable range in $\bar{\epsilon}$ in the absence of tunneling have been made. Using a simplified model for a hydrogen-transfer reaction, Swain and coworkers (23) obtained a value of 1.442, considering only zero-point-energy effects.

Bigeleisen (24), using a more complete model, proposed a range of 1.33–1.58 for the relative isotope effects, including Wigner tunneling (valid if κ is close to unity). He stated that extensive tunneling should lead to abnormally low values of $\bar{\epsilon}$. More O'Ferrall and Kouba (25) calculated isotope effects for some model proton-transfer reactions involving linear four- and five-atom transition states. They found deviations of only 2% from the Swain value of $\bar{\epsilon}$ (1.442), even when tunneling corrections for a parabolic barrier were included. It has also been shown by Lewis and Robinson (26) that tunneling corrections do not necessarily produce significant changes in the relative isotope effect.

Recently, Stern and Vogel (27) investigated relative tritium-deuterium isotope effects for 180 model reaction systems. They found that, within the temperature range 20–1000°K, $\bar{\epsilon}$ was restricted to the range $1.33 \leq \bar{\epsilon} \leq 1.58$ provided that:

1. k_H/k_T and k_H/k_D reflect significant force-constant changes between reactant and transition state at the isotopic position(s).

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2. k_H/k_T and k_H/k_D are both greater than unity.

3. k_H/k_T and k_H/k_D exhibit "regular" temperature dependences at all temperatures, "regular" being defined in their paper.

Stern and I (28) re-examined the model reactions meeting the above three criteria, to see what effect the inclusion of tunneling would have on the relative isotope effect. The tunneling corrections were calculated as described in the preceding sub-section. Although this was done for a large number of model reactions, I shall discuss here only the model for hydrogen-atom abstraction that has already been mentioned in the preceding sub-section. Again, two variations were considered: in one, $V_H^* = V_D^* = V_T^*$; in the other, $V_D^* = V_H^* + 1$, $V_T^* = V_H^* + 1.45$. Figs. 8a and 8b show the ratios of tunneling corrections, $\Gamma_H^*/\Gamma_D^* \equiv T_{H/D}$ and $\Gamma_H^*/\Gamma_T^* \equiv T_{H/T}$, for the two cases. In addition, the relative tritium-deuterium tunneling correction

$$\underline{t} \equiv \ln T_{H/T} / \ln T_{H/D}$$

is indicated. The slightly different shapes of $\ln T_{H/T}$ and $\ln T_{H/D}$ vs. $\log T$ result in a temperature dependence of $\underline{t}$. At high temperatures, Γ^* is given by the Wigner expression, and it can be shown (24) that

$$\underline{t} \rightarrow \frac{1 - (v_T^*/v_H^*)^2}{1 - (v_D^*/v_H^*)^2} \quad \text{as } T^{-1} \rightarrow 0$$

If the barrier height depends on isotopic substitution, there is a temperature at which $T_{H/T}$ is unity and $\underline{t}$ is zero. At a slightly higher temperature, $T_{H/D}$ becomes unity and $\underline{t}$ has a pole (∞).

The relative isotope effect including the tunneling correction, which we designate as $\underline{r}'$, can be expressed in terms of $\underline{r}$ and $\underline{t}$, the relative isotope effect without tunneling:

$$\underline{r}' = \frac{\ln R_{H/D}}{\ln R_{H/D}'} \underline{r} + \left(1 - \frac{\ln R_{H/D}}{\ln R_{H/D}'} \right) \underline{t}$$

In this expression, $R_{H/D}$ is the rate constant ratio with no tunneling correction, and $R_{H/D}'$ the same ratio including tunneling. It is apparent that the weighting factors multiplying $\underline{r}$ and $\underline{t}$ are complementary; as a result, plots of the weighted $\underline{r}$ and weighted $\underline{t}$ contributions vs. $\log T$ will be, approximately, displaced "mirror images" (cf. Figs. 8a' and 8b'). Because the two contributions are not exactly out of phase, a slight temperature dependence of $\underline{r}'$ remains. Fig. 9 illustrates the effect on $\underline{t}$ and on $\underline{r}'$ of

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changes in V^* ; note that deviations of $\underline{x}'$ vs $\log T$ from a smooth, monotonic curve increase as the barrier height increases.

The important point, however, is that even when tunneling is very significant (cf. legend at top of Fig. 9), $\underline{x}'$ does not greatly exceed the "nontunneling" range of 1.33-1.58. Furthermore, contrary to the assumptions of earlier authors, $\underline{x}'$ drops below the lower limit only for the highest barrier tested, and over a narrow temperature range. Although tunneling is important at these temperatures, the tunneling correction is even larger at lower temperatures where $\underline{x}'$ exceeds the upper range of 1.58. Except for the lowest barrier, where relative differences between V_H^* , V_D^* , and V_T^* are large, the conclusions for the case when the barrier height is isotope-dependent are very similar. Note that the abnormal behavior of $\underline{x}$ in Fig. 8b and 9b is removed by the weighting factor to give the smooth curves of Figs. 8b' and 9b'. The only cases for which the discontinuity in $\underline{x}'$ is retained are physically unrealistic models in which secondary isotope effects are combined with an isotope-dependent barrier height.

The large number (~ 60) of other model reaction systems we investigated all gave results qualitatively similar to those discussed above, but with subtle differences dependent on the particular model. We conclude from this work that:

1. Even when quantum-mechanical tunneling is important, the limits $1.33 \leq \underline{x} \leq 1.58$ are not likely to be exceeded, if they would not be exceeded in the absence of tunneling.

2. There is no general correlation between the magnitude of $\underline{x}$ and the importance of tunneling.

3. The temperature dependence of $\underline{x}$ is qualitatively the same for a wide range of barrier heights and reaction models.

Experimental data for some systems in which both deuterium and tritium isotope effects have been measured are given in Table I. Again, the warning must be issued that other reactions undoubtedly exist in which tunneling is important but has not been searched for by this method. Nevertheless, there is only one reaction listed (No. 7) where the experimental value of $\underline{x}$ is significantly outside the range of 1.33-1.58. Interestingly, the temperatures at which this reaction was studied are close to the temperature at which a minimum value of $\underline{x}'$ is calculated from the model discussed above.

Conclusion: What About Chemical Principles?

I hope that the details of the preceding sections have not diverted the reader's attention from the general subject of this

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50 symposium: "Isotopes and Chemical Principles". Let me reiterate
49 the principle that underlies these details:
48

47 *Classical mechanics cannot be relied upon to provide an*
46 *adequate and accurate description of the motion of light atoms*
45 *(particularly isotopes of hydrogen) during a chemical reaction.*
44 *The wave nature of the moving particle must be taken into account*
43 *because it permits "tunneling" through the potential energy*
42 *barrier separating reactants from products. Because the wave-*
41 *length (and hence the extent of tunneling) of the moving atom is*
40 *mass-dependent, kinetic isotope effects will reflect this wave-*
39 *mechanical property.*
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37 Unfortunately, the diagnostic methods that have been used to
36 search for tunneling in actual experiments have not led to un-
35 equivocal proof. In effect, the foundation is solid, but the
34 structure that has been built on it is somewhat rickety. Antici-
33 pated developments that will improve the sturdiness of this
32 structure over the next few years are:
31

- 30 1. The calculation of accurate potential energy surfaces
29 for reacting systems consisting of a few atoms.
28
- 27 2. Complete wavenmechanical calculations, with these
26 potential energy surfaces, of reactive cross
25 sections and other details of reaction dynamics.
24
- 23 3. Precise measurements of cross sections for these
22 reaction systems, with reactants in well-defined
21 states.
20

19 Acknowledgement

18

17 The tragic death of Marvin Stern brought to an untimely end
16 the promising career of a good friend and respected colleague.
15 His contributions to our calculations described here and in more
14 detail elsewhere (22,28) cannot be overestimated. To this work
13 he brought his insight into the significant features of the
12 problem and his uniquely high standards of meticulous attention
11 to detail.
10

9 This paper is based on research supported by the U. S. Atomic
8 Energy Commission.
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Table I. Arrhenius Preexponential Factors and Relative Tritium-Deuterium Isotope Effects

Reaction	A_Q	k	Ref.
1. 4-Nitrophenylnitromethane + tetramethylguanidine (in toluene)	0.032	-	a
2. Same reaction in dichloromethane	0.45	-	a
3. Leucocystal violet + chloranil	0.04	1.31	b
4. 2-Carbethoxycyclopentanone + F^-	0.042	1.32	c,d
5. 2-Nitropropane + 2,4,6-trimethylpyridine	0.15	1.39	b
6. Oxidation of 1-phenyl-2,2,2-trifluoroethanol	0.25	1.46	b
7. 2-Carbethoxycyclopentanone + chloracetate ion	0.35	1.72	c,d
8. Acetophenone + OH^-	0.38	1.38	e
9. 1-Bromo-2-phenylpropane + ethoxide	0.40	1.48	f,g
10. 2-Carbethoxycyclopentanone + D_2O	0.44	1.48	c,d
11. Pyridinediphenylborane + H_2O	0.94	1.38	h
12. 2,2-Diphenylethylbenzene-sulfonate + methoxide	1.1	1.48	i

^aRef. 19^bRef. 26^cBell, R. P., Fendley, J. A., and Hulett, J. R., Proc. Roy. Soc. Ser. A (1956), 235, 453.^dJones, J. R., Trans. Faraday Soc. (1969), 65, 2430.^eJones, J. R., *ibid.* (1969), 65, 2138.^fShiner, V. J., Jr. and Smith, M. L., J. Amer. Chem. Soc. (1961), 83, 593.^gShiner, V. J., Jr. and Martin, B., Pure Appl. Chem. (1964), 8, 371.^hLewis, E. S. and Grinstein, R. H., J. Amer. Chem. Soc. (1962), 84, 1158.ⁱWilli, A. V., J. Phys. Chem. (1966), 70, 2705.

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line**Figure Captions**

1. Permeability of a barrier to a particle with kinetic energy less than barrier height. The dashed line represents the wave function for a particle of energy E moving from the left and interacting with an Eckart barrier (solid line) (29).
Reprinted with permission from D. L. Bunker - THEORY OF ELEMENTARY GAS REACTION RATES. Copyright 1966, Pergamon Press Ltd., Oxford.
2. Transmission probability $\kappa(\epsilon)$ as a function of reduced energy $\epsilon (=E/V^*)$ and $\alpha (=2\pi V^*/h\nu^*)$ for a symmetrical Eckart barrier (30).
Reprinted with permission from Harold S. Johnston - GAS PHASE REACTION RATE THEORY, Copyright 1966, The Ronald Press Company, New York.
3. Hypothetical potential energy surface for the collinear reaction $A + BC \rightarrow AB + C$. The solid lines are equipotentials and the dashed line is the reaction path (31).
From Ralph E. Weston Jr. and Harold A. Schwarz - CHEMICAL KINETICS, 1972. Reprinted by permission of Prentice-Hall, Inc., Englewood Cliffs, New Jersey.
4. Rate constant ratio k_H/k_D for the abstraction of H or D from CHD_3 or CH_2D_2 . The points are experimental values, and the lines are values calculated from different reaction models. (a) No tunneling correction included, (b) Tunneling correction included. (18).
5. Qualitative portrayal of the temperature dependence of an isotopic rate constant ratio in a reaction where tunneling is important. The Arrhenius intercept which would be obtained at high temperatures ($A_{Q,\text{class}}$), and the intercept obtained by extrapolation from low temperatures (A_Q) are indicated.
6. Arrhenius-type plots of Γ_H^* , Γ_D^* , Γ_H^*/Γ_D^* and $(k_H/k_D)_{\text{class}}$ for a model hydrogen-atom abstraction with (a) $V_H^* = V_D^* = 10$ kcal/mole, (a') $V_H^* = 10$, $V_D^* = 11$ kcal/mole (22).
7. Arrhenius pre-exponential factors as functions of temperature for a model hydrogen-atom abstraction with various barrier heights: (a), tunneling correction only, $V_D^* = V_H^*$; (a'), complete isotope effect, $V_D^* = V_H^*$; (a''), complete isotope effect, $V_D^* = V_H^* + 1$. The curves are labeled with V_H^* in kcal/mole. (NT indicates that no tunneling correction is included.) Numbers at the top of each graph are $\ln \Gamma_H^*$ for $V_H^* = 10$, as a function of T_{avg} . Dashed lines are at $A_Q = \frac{1}{2}$ and $\sqrt{2}$ (22).

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- 50 8. Relative tritium-deuterium kinetic isotope effect r' and
 49 individual contributors to r' for a model hydrogen-atom
 48 abstraction: (a),(a'), $V_H^* = V_D^* = V_T^* = 10$ kcal/mole;
 47 (b),(b'), $V_H^* = 10$, $V_D^* = 11$, $V_T^* = 11.45$ kcal/mole (28).
 46
- 45 9. Relative tritium-deuterium kinetic isotope effects as functions
 44 of temperature with various barrier heights: (a),(b), tunnel-
 43 ing only; (a'),(b'), complete isotope effect. Unprimed letters
 42 are for isotope-independent barrier heights and primed letters
 41 are for $V_D^* = V_H^* + 1$, $V_T^* = V_H^* + 1.45$ kcal/mole. The curves
 40 are labeled with V_H^* in kcal/mole. Numbers at the top of the
 39 graphs are $\ln f_H^*$ for $V_H^* = 10$ kcal/mole, as a function of $\log T$.
 38 Dashed horizontal lines are the "nontunneling limits", 1.33 and
 37 1.58. The infinite-temperature limit of the relative isotope
 36 effect is indicated by "n" at right border (28).
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Fig 4a

Fig 4b

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Fig. 5

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Fig. 9