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ELECTRON AND NUCLEAR TUNNELING IN CHEMICAL AND BIOLOGICAL SYSTEMS

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The characteristics of electron tunneling and of nuclear tunneling are distinguished, and criteria for identifying each are considered. Examples are drawn from simple electron transfer systems, and the results together with those on nuclear rearrangements are used to analyze several reactions in photosynthetic systems. The relation of nuclear tunneling in certain systems to the energy gap law in radiationless transitions is described.

I. INTRODUCTION

In the present paper we consider conditions under which electron tunneling, nuclear tunneling, or both may contribute to chemical reactions, including those in biological systems. In Section II theoretical concepts involved in electron transfers are outlined, together with various arrangements of the potential energy surfaces (Figs. 1-4). The differences and effects of electron and nuclear tunneling are described in Section III, and examples are given in Section IV. An analysis of some reactions in biological systems is given in Section V. In conclusion, some remarks on similarities and differences from proton transfers are given in Section VI.

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II. THEORETICAL CONCEPTS

In treating electron transfer reactions and recognizing the nuclear rearrangements which facilitate them, it is convenient to consider the potential energy of the entire system (the two reactants plus surrounding environment) as a function of all the nuclear coordinates in the system (1-5). Some 10^{23} coordinates are involved, and so it is useful for pictorial purposes to give a profile of such a plot, labelled R in Figure 1. A profile of a similar plot for the two products plus environment is labelled P there. The abscissa represents some path in the many-dimensional nuclear coordinate space leading from atomic configurations appropriate to the stability of the reactants to those appropriate to the stability of the products.

The coordinates in this space typically involve all bond lengths bond angles, and orientations of the reactants and of the molecules of the environment. Thus, the abscissa in Figure 1 involves some concerted combination of all of these different coordinates.

When the reactants are sufficiently far apart, there is a negligible probability of electron transfer, and the relevant potential energy curves are as depicted in Figure 1. This plot needs to be modified when the reactants are closer, for then an electronic coupling between them occurs and particularly modifies the curves in the vicinity of the crossing point.[1] One obtains the well-known quantum mechanical splitting, as in Figure 2.

In Figure 1, where no electronic interaction occurs, a system on the potential energy surface R remains on that surface no matter what fluctuations the nuclear coordinates of the system undergo. When, however, the reactants are closer together, so that the R and P surfaces are as in Figure 2, a suitable fluctuation of nuclear

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[1] *W.F. Libby (5) made the stimulating suggestion that the Franck-Condon principle should be applicable to electron transfer reactions The description in terms of potential energy surfaces provides a way of visualizing this principle and its implications.*

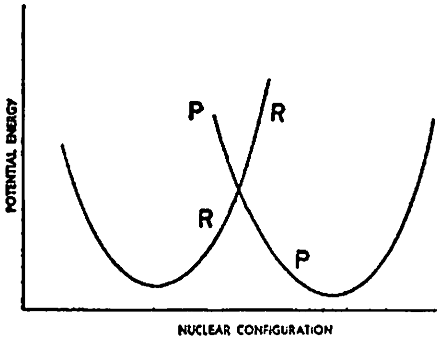

FIGURE 1. *Profile of a plot (see Refs. 1-5) of the potential energy of the system of reactants plus environment (R) and products plus environment (P) versus the configuration of the nuclei of the entire system. The plot is made for an approximately thermoneutral reaction, and for the case of no electronic interaction between the reactants.*

coordinates permits a system originally on R to go over to the lower P surface when the system passes through the "intersection" region; i.e., it can stay on the lowest surface in the Figure.

When the system passes through this intersection region the probability for any given energy E that it moves from the R to the P surface can be calculated by a Landau-Zener transition probability expression, $\kappa(E)$ (see Refs. 6,7).[2] When the splitting in Figure 2 is sufficiently large, this $\kappa(E)$ is unity for systems which have enough thermal energy E to overcome the barrier in Figure 2. When the splitting, on the other hand, is very small, the transition probability becomes small, even for such E's, and varies as the square of some electronic coupling matrix element.

We consider with these figures in mind the properties of electron tunneling and nuclear tunneling (1-5). The electron tunneling rate is reflected in the extent of the splitting ΔE of the R and P

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[2] *For a test of the formula for w(E), even in the tunneling regime, see Figure 7 for the strong coupling region and Equations (4.12) and (4.16) of Nikitin (6). In the symbol w(E) used in the present text for brevity, the E is really that part of E along the reaction coordinate, i.e., along the abscissa in Figures 2 to 4.*

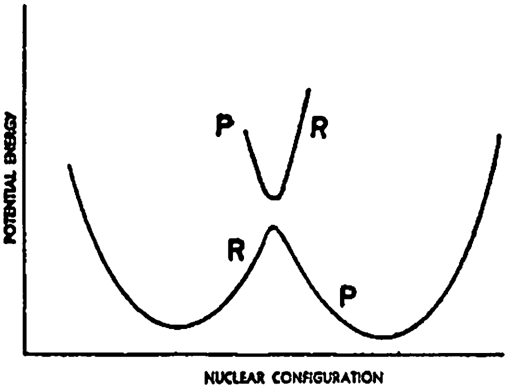

FIGURE 2. Same as in Figure 1, but for a finite electronic coupling.

surfaces in Figures 2 and 3, being of the order of $\Delta E/h \cdot sec^{-1}$. The effective barrier to this tunneling is not depicted in Figures 2 or 3, nor do we need it to calculate the transition probability, κ, the appropriately weighted value of $\kappa(E)$: the properties of the surfaces at the intersection region, with the aid of a quantum mechanical expression such as that of Landau and Zener, permit the calculation of κ.

When the splitting is very small, κ is also small, and the reaction is said to be electronically nonadiabatic. When the splitting is large, κ is close to unity and the reaction is termed adiabatic and the concept of an electron "tunneling" is not useful to describe κ. A key question is whether reactions are

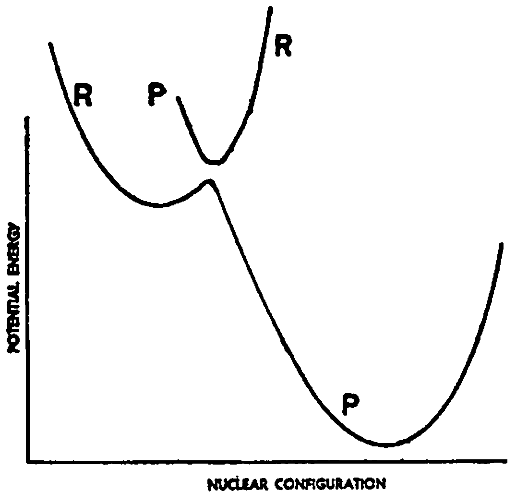

FIGURE 3. Same as in Figure 2, but for a very exothermic reaction.

electronically adiabatic or nonadiabatic, and we shall consider a criterion for establishing this aspect of the electron transfer.

Nuclear tunneling occurs in Figures 2 and 3 when the energy is below the potential energy maximum of the lower surface. In this instance at low enough temperatures the reaction ultimately becomes independent of temperature: all systems react from their lowest vibrational state or states, and at low enough temperatures the probability of finding the system in that state is essentially temperature-independent.

We shall need in our discussion of some biological systems still another figure. When the reaction is "downhill," i.e., exothermic, the P surface in Figure 2 is lowered, as in Figure 3. The barrier is then less and the reaction is therefore faster. This behavior has been described quantitatively and explored at length experimentally for simple inorganic, organic, and electrochemical systems (8-11). (Figures 1-3 effectively apply to electrochemical systems also.) When the reaction is highly exothermic, and when at the same time the difference in equilibrium nuclear configuration (horizontal distance between minima) is small, e.g., the difference in each bond length in a reactant and the same bond length in a product is small, as in Figure 4, either the R and P surfaces may no longer cross or they will cross only at a very high energy.

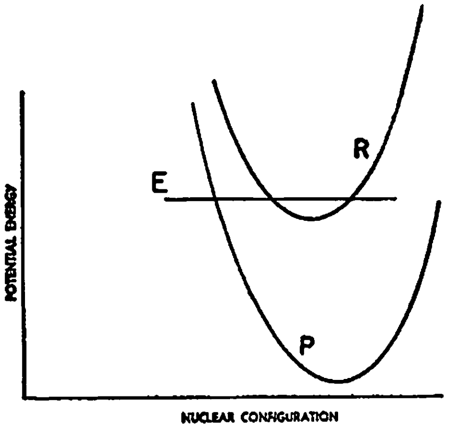

FIGURE 4. Same as in Figure 2, but for a very exothermic reaction that, at the same time, has a small difference in stable configurations of reactants and products.

A situation where nuclear tunneling can occur is illustrated in Figure 4. In this case, even at room temperature, such a system reacts by nuclear tunneling, either because there is no crossing of the R and P curves or because the "intersection" point is energetically relatively inaccessible. In this case the electronic couplinq could still be either strong or weak, and its strength would affect the electron transfer rate.

The quantitative aspects for systems such as the one in Figure 2 have been recently reviewed elsewhere (8-11). It has been possible, for example, to predict the rates of "cross-reactions" between two redox systems 1 and 2,

$$Ox_1 + Red_2 \xrightarrow{k_{12}} Red_1 + Ox_2 \qquad (1)$$

from the self-exchange rate constants,

$$Ox_1 + Red_1 \xrightarrow{k_{11}} Red_1 + Ox_1 \qquad (2)$$

$$Ox_2 + Red_2 \xrightarrow{k_{22}} Red_2 + Ox_2 \qquad (3)$$

and the equilibrium constant of Reaction (1), K_{12},

$$k_{12} \approx (k_{11}k_{22}K_{12}f)^{1/2} \qquad (4)$$

where f is a known function of k_{11}, k_{22}, and K_{12}. This relation has been extensively investigated and applied in the literature and is discussed in the above reviews (8-11).

Various aspects of the theory (1-5) investigated include the *ab initio* calculation of rate constants, as discussed in Dr. Sutin's paper in this symposium, the effects of solvent medium when that solvent doesn't alter the coordination shell, the relation between homogeneous electron transfer rates and the rates of related reactions at electrode surfaces, the effect of the standard free energy of reaction of an electron transfer step on the rate of that step, and other properties. A review of some of this material is given elsewhere (8-11), and to avoid repetition will not be described

From Figures 2 and 3 one sees that initially the potential energy barrier (potential energy at the "crossing point" minus that at the minimum of the R curve) decreases with increasing reaction exothermicity. However, as one sees from Figure 4, the effective barrier *increases* with increasing exothermicity (1,12-14) at sufficiently high exothermicities, because (a) the "intersection" occurs only at high energies (1,12,13),[3] and (b) when tunneling occurs, the tunneling distance at any energy E increases as the P is lowered still further (14),[4] i.e., when the exothermicity is increased. This prediction receives some support from a recent experimental study by Sutin and Creutz (21).

When nuclear tunneling occurs, i.e., when (b) occurs, the decrease of rate with increasing exothermicity at sufficiently large exothermicities is more gradual (14) than when reaction occurs via (a), the intersection case (1,12,13); the rate varies exponentially with the first power of the exothermicity instead of with the second power. The first power behavior is well known in the field of radiationless transitions, where the phenomenon is known as the energy gap law (22-26).

We shall later invoke this behavior of decreasing rate with increasing exothermicity in highly exothermic systems to explain a result in biological electron transfers. For the moment, however, we note from Figure 4 that the physical origin of the behavior in (b) above is clear: the greater the vertical difference in the minima of the R and P curves, the greater will be the nuclear tunneling distance from the R to the P curve at any fixed energy E, and hence the smaller will be the reaction rate; similarly, in (a) the higher will be the "intersection" point, if any, and so the higher will be the energy barrier.

This behavior can also be understood in terms of Franck-Condon vibrational overlap integrals: the greater this vertical distance,

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[3] *Nuclear tunneling is neglected in these references.*

[4] *For related quantum treatments see References 15-20.*

the greater will be the oscillations of the vibrational wavefunction of the P system at the energy E and the smaller will be the overlap integral with the vibrational wavefunction of the R system at the same total energy E. A semiclassical evaluation of this overlap integral then leads to descriptions (a) and (b) given above.

We turn next to criteria for recognizing electron and/or nuclear tunneling.

III. ELECTRON AND NUCLEAR TUNNELING RECOGNITION

A. *Electron Tunneling*

The rate constant k_r of an electron transfer reaction can be written as

$$k_r = A\cdot\exp(-E_a/kT) \tag{5}$$

where E_a is the activation energy. A is a pre-exponential factor of the order of 10^{13} sec^{-1} for first-order reactions, 10^{11} M^{-1} sec^{-1} for second-order reactions, and 10^4 cm$\cdot$ sec^{-1} for reactions at electrodes, multiplied in each case by $\kappa\cdot\exp(\Delta S^*/k)$ (see Refs. 1-5). Here κ is a Landau-Zener type transition probability for going from curve R to curve P in the "intersection" region, suitably weighted over various translational and vibrational states. ΔS^* is the entropy of activation due to any loss or gain in rotational - vibrational freedom of the system. Thus,

$$A \quad 10^{13}\ \kappa\cdot\exp(\Delta S^*/k)\cdot\mathrm{sec}^{-1}\ \text{(first-order)} \tag{6}$$

$$A \quad 10^{11}\ \kappa\cdot\exp(\Delta S^*/k)\cdot M^{-1}\ \mathrm{sec}^{-1}\ \text{(second-order)} \tag{7}$$

$$A \quad 10^{4}\ \kappa\cdot\exp(\Delta S^*/k)\cdot\mathrm{cm}\cdot\mathrm{sec}^{-1}\ \text{(electrode reaction)} \tag{8}$$

When the electron tunneling rate is very small and when nuclear tunneling is absent, κ is small, and so when $\Delta S^* \simeq 0$ we shall have $A \ll 10^{13}$ sec^{-1} and $A \ll 10^{11}$ M^{-1} sec^{-1} in the first- and second-order cases, respectively. Because of these assumptions of no nuclear tunneling and $\Delta S^* \simeq 0$, some care must be exercised in concluding from a small value of A the presence of a slow electron tunneling rate. Accordingly we turn next to one of these questions, nuclear tunneling.

B. Nuclear Tunneling

A typical manifestation of nuclear tunneling is seen from the temperature behavior: when the reaction rate constant k_r displays an activation energy in one temperature range and tends to become temperature-independent at lower temperatures, one has evidence of nuclear tunneling through the barrier, as in Figure 2.[5] We have also already noted that in Figure 4 one has nuclear tunneling even at room temperature. Unless the intersection region (if any) is reasonably accessible energetically, it is possible that the k_r for this system will be largely temperature-independent at conveniently accessible temperatures.

IV. EXAMPLES OF ELECTRON AND NUCLEAR TUNNELING

We consider examples of the A factor in Equation (1). In the MnO_4^- - MnO_4^{2-} exchange reaction (27,28)[6], when ΔS^* is calculated from a dielectric continuum expression, $A \cdot \exp(-\Delta S^*/k)$ is of the order of 10^{11} M^{-1} sec^{-1}, give or take a factor of 10. So here, the κ in Equation (7) is of the order of unity or perhaps 0.1. For reactions such as Fe^{2+} - Fe^{3+}, the product of the ionic charges is some three times larger, and ΔS^* is also. The calculation of κ from $A \cdot \exp(-\Delta S^*/k)$ is therefore somewhat more uncertain, since the dielectric continuum theory is probably somewhat more uncertain for systems of large ionic charges. Nevertheless, results

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[5] *To be sure, some curvature in the Arrhenius plot of* $\ln k_r$ *vs.* $1/T$ *at lower T's could be due to other reasons in the threshold energy region for reactions. However, a temperature independence at sufficiently low T, and an activation energy at high T, is rather clear evidence for nuclear tunneling at the low T's.*

[6] *The data in these references were used, together with an estimate of* ΔS^* *from electrostatic continuum arguments.*

by Dr. Sutin in this symposium indicate a rather small κ in this way. A's for various electron transfers at electrodes measured in high salt concentration (29) where the ΔS^* due to electrostatic effects is presumed small, were about 10^3 to 10^5 cm·sec^{-1}, close to the theoretical value of 10^4 cm·sec^{-1} for such systems [see Eq. (8)]. Thus, for them κ is of the order of 1, again give or take a factor of 10. The self-exchange reaction between an aromatic molecule and its anion is very rapid (30), close to diffusion control. The value is reasonably well accounted for (30) by the solvent reorganization energy, reflecting the reorientation of solvent molecules occurring along the abscissa in Figure 2. Thus, in this case κ is probably close to unity also. Again, the $Fe(phen)_3^{2+} - Fe(phen)_3^{3+}$ reaction is very fast, just below diffusion control (31)[7], and so one expects that κ is again of the order of unity to 0.1. In a ruthenium system, Dr. Sutin obtains good agreement between experiment and theory by assuming adiabaticity, i.e., assuming $\kappa \simeq 1$.

Thus, in such cases, apart from the $Fe^{2+} - Fe^{3+}$ system, κ appears to be of the order of unity, to within a factor of 10 or so, and so these reactions would therefore be more or less adiabatic (within this factor) and the electron tunneling concept is less useful, i.e., electron tunneling does not contribute more than this factor to the slowness of the reaction in these cases. When the system reaches the intersection region in Figure 2, it tends to remain on the lowest potential surface there and so react $\gtrsim 0.1$ of the time for those systems.

We consider next nuclear tunneling. Reactions are usually not studied at the extremely low temperatures that Drs. DeVault and Chance (33-35, and pers. comm.), Frauenfelder and co-workers, and Goldanskii used in their respective experiments (This Symposium).

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[7] *Corrected for diffusion control, the rate constant is* 2×10^9 M^{-1} sec^{-1}*, the diffusion control rate constant for this system being about* 3.3×10^9 M^{-1} sec^{-1} *(see also Ref. 32).*

Their observation of a temperature-dependent rate constant at higher temperatures and a temperature-independent one at low temperature reflects the occurrence of nuclear tunneling at the low temperatures. More typical in chemistry are the studies at not-so-low temperatures, and here a deviation from linearity of the Arrhenius plot of ln k_r vs. 1/T is taken as evidence. More commonly, the existence of large isotope effects using H, D and T in the case of proton transfer reactions is the usual evidence for nuclear tunneling, since otherwise it is difficult to account for the size of the large isotope effects (36,37).

Another example of tunneling occurs in radiationless transitions, in the case of the energy gap law even at room temperature, as we have already discussed (22-26).

V. ELECTRON TRANSFER IN BIOLOGICAL SYSTEMS

The sequence of electron transfer reactions which we shall consider are in the bacterial photosynthetic system,[8] wherein an electronic excitation of a bacteriochlorophyll dimer $BChl_2$ is presumed to occur after light absorption and excitation transfer in the system. This excitation is followed by an electron transfer to bacteriopheophytin BPh, and then to an iron-ubiquinone acceptor, X, with the indicated half-lives:

$$BChl_2^* + BPh \rightarrow BChl_2^+ + BPh^- \qquad \tau \lesssim 10 \text{ psec} \tag{9}$$

$$BPh^- + X \rightarrow BPh + X^- \qquad \tau \approx 150 \text{ psec} \tag{10}$$

$$X^- \rightarrow \text{etc.} \tag{11}$$

When the X is already reduced before the formation of $BChl_2^*$, one has instead of Equation (10) some back reactions to form a triplet and the ground state singlet of $BChl_2$:

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[8] *See Reference 38, and also references cited therein. This article summarizes recent data.*

$$BPh^- + BChl_2^+ \rightarrow BPh + BChl_2^{*T} \qquad \tau \approx 10 \text{ ns} \qquad (12)$$

$$BPh^- + BChl_2^+ \rightarrow BPh + BChl_2 \qquad \tau \approx 10 \text{ ns} \qquad (13)$$

Following reactions (10) and (11), the chlorophyll dimer cation, $BChl_2^+$, is neutralized by an electron from cytochrome *c* (31,32):

$$\text{cyt } c^{II} + BChl_2^+ \rightarrow \text{cyt } c^{III} + BChl_2 \qquad \tau \approx 1\ \mu\text{sec} \qquad (14)$$

where the value of $\tau \approx 1$ μsec is cited for the reaction in *Chromatium* with a low potential cytochrome *c* (31,32). (The other values are cited for *Rps. sphaeroides*.)

We shall consider the questions of nuclear and electron tunneling and nuclear rearrangement for these reactions.

Reaction (9) is seen to be extremely fast. Were it a factor of ≲100 faster it would have a $k_r \approx 10^{13}$ sec^{-1}, the theoretical maximum. From the studies of electron transfer rates between an aromatic molecule and its anion and between $Fe(phen)_3^{2+}$ and $Fe(phen)_3^{3+}$ referred to earlier (30-32), one would expect very little rearrangement of bond lengths and very little barrier to reaction in these highly aromatic systems, and thus very little activation energy. The barrier in References 30-32, such as it is, is probably due to reorientation of the polar solvent molecules, but it is small because of the large size of the aromatic systems. In the membrane there are presumably less polar groups in the vicinity of the reactants in (9), and so there would be even less reorientation of polar groups than in the above aromatic systems. So, in the absence of other effects, reaction (9) should be very rapid.

If the R and P curves for reaction (9) are, for the above reasons (smallness of nuclear rearrangement), situated almost over each other, one would need nuclear tunneling in order to reach curve P from curve R, giving rise to a $\kappa < 1$ in Equation (6). Such a behavior would have little temperature dependence, as compared with that for the case where the R and P curves "intersect" some distance above the minimum of the R curve.

If the reactants in (9) were situated quite some distance apart the electron tunneling rate would be small, again giving rise to a κ <<1 and a largely temperature-independent rate. At this time the experiments haven't distinguished between these three possibilities: (a) a smallness in κ (≤0.01) due to a slowness in nuclear tunneling, (b) a smallness in κ (≤0.01) due to a slowness in electron tunneling, and (c) a little rearrangement leading to a slight activation energy. A measurement of the temperature dependence would tend to distinguish (c) from (a) and (b).

Reaction (10) is about fifty times slower, but remarks analogous to the above apply. Reactions (9) and (13) provide an interesting comparison with each other. If the geometry, e.g., separation distance and mutual orientation of reactants, is the same for both, then the fact that (13) is some 1000-fold slower than (9) is at first glance perhaps puzzling, until one looks at the exothermicities. The mid-point potential of the $BChl_2^+$-$BChl_2^-$ couple is about 0.45 volts [(39,40) and references cited in (40)]. The absorption and fluorescence spectra have maxima at 863 nm and 902 nm, respectively (41), corresponding to 1.44 and 1.38 volts. Thus, the minima of the $BChl_2$ and $BChl_2^*$ curves are separated vertically by about 1.41 volts, which yields a mid-point potential of the $BChl_2^+$-$BChl_2^*$ couple of -(1.41-0.45), i.e., -0.96 volts. The mid-point potential of the BPh-BPh^- couple (42)[9] is about -0.4 volts. Accordingly, Reaction (9) is 0.56 volts downhill, and Reaction (13) is 0.85 volts downhill. Thus, the slowness of (13) relative to (9) may reflect the energy gap law - and the added resulting nuclear tunneling needed to go from the R to the P curve - discussed in Section II.

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[9] *The value in Reference 42 is given for* in vitro *BPh/BPh⁻. The* in vivo *value for* Rps. sphaeroides *is not yet known.* In vivo *estimates for* Rps. viridis *have been made by Prince* et al. *(43) and by Kliminov* et al. *(44), giving values of -0.40 and -0.62 V, respectively.*

Reaction (10) is also quite downhill, about 0.35 volts, since the mid-point potential of X-X^- is about -0.05 volts.[10] Its slowness relative to Reaction (9) presumably reflects other factors.

Reaction (12) is probably slow for reasons different from the exothermicity-induced slowness of (13), since (12) would not be very exothermic. This reaction and the influence of applied magnetic fields have been discussed by several researchers [(46-48) and references cited in (48)]. The radicals BPh^- and $BChl_2^+$ are formed in a singlet state, and the triplet state can be formed in (12) as a result of hyperfine interaction with the nuclear spins. A characteristic frequency for this interaction is of the order of the rate corresponding to 10 ns (R. Haberkorn and M.E. Michel-Beyerle, pers. comm.).

Reaction (14) is still slower. The activation energy of this reaction in the room temperature range has been measured (33,35) ($E_a \simeq 5$ Kcal•mole^{-1}), and its presence reflects an appreciable reorganization which accompanies the reaction. The non-zero activation energy also indicates that the minima of the R and P curves for this reaction are appreciably displaced from each other along the abscissa, so that the curves can intersect even though the reaction is quite exothermic. The slowness of Reaction (12) also probably reflects the slowness of the cytochrome *c* self-exchange reaction in solution (49).[11] The value of A in Equation (5) for Reaction (14) at room temperature is of the order of 5×10^9 sec^{-1}, well below the 10^{13} sec^{-1} value (33-35). Presuming nuclear tunneling at room temperature to be minor, the small A value could arise (a) because the electronic tunneling rate may be slow, particularly since there appears to be a very large

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[10] *In* Rps. viridis *the separation distance of* BPh^- *and X is small enough for spin-spin dipolar effects to be observed; see Prince* et al. *(43,45).*

[11] *The effect of transmembrane potentials on the cytochrome* c_2 *reaction center equilibrium in* Rps. sphaeroides *has been determined by Takamiya and Dutton (50), and analogous effects should be considered in the other reactions.*

separation distance between the reactants in Reaction (14) (see Ref. 38), and (b) because of possible entropic effects, as indicated by the ΔS^* term. A knowledge of ΔS° for this reaction, if not already available would be desirable.

VI. PROTON TRANSFER REACTIONS

We conclude with some brief remarks on proton transfer reactions, reactions which occur later in the photosynthetic chain. The question has frequently been asked whether the formalism derived for electron transfer reactions can be applied to proton transfers: both electrons and protons are light-weight particles, and the Franck-Condon arguments used for electron transfers might be conjectured to apply to proton transfers. Recently, an answer to this question was given in terms of the relevant potential energy surface (51). Only a brief summary of the results will be given here.

A proton transfer,

$$A\text{-}H^+ + B \rightarrow A + B\text{-}H^+ \qquad (15)$$

is conveniently described in terms of a potential energy surface as a function of the various distances, such as the length of the $A\text{-}H^+$ bond and the distance between B and the center of mass of $A\text{-}H^+$, as in Figure 5.[12] The surface in Figure 5 is given for a fairly thermoneutral reaction. The surface has a saddle-point, which occurs near a symmetrical configuration for this case, if $A\text{-}H^+$ and $B\text{-}H^+$ are of rather similar bond length and vibration frequency. (Line X in Fig. 5 crosses the saddle-point). At such a saddle-point the two valleys in the surface (corresponding to stable $A\text{-}H^+ + B$ and $A + B\text{-}H^+$ systems, respectively) have merged. If the proton transfer occurs when the system passes near this saddle-point, namely near line X in Figure 5, there is no applicability of the weak-overlap (perturbation theory) Franck-Condon concepts of electron

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[12] *See Glasstone* et al. *(52) for skewed-axes diagrams.*

transfer, since the two channels have merged. When, instead, the proton transfer occurs before the saddle-point region is reached, e.g., near line Y in Figure 5, the mechanism depends on the vibrational energy: if the vibrational energy of the A-H$^+$ vibration is, for all paths Y, less than the potential energy barrier for proton transfer to the other channel, there will be a clasically-nonallowed transition, namely a nuclear tunneling. There will be a classically-nonallowed transition if the vibrational energy of A-H$^+$ for some path Y exceeds the potential energy barrier at that Y. In the case of weak electronic interaction between the two channels the usual Franck-Condon approach could be used, and there is then a strong similarity to the usual weak overlap electron transfer case. However, in the much more likely case, for proton transfers, of strong electronic interaction, the weak-overlap Franck-Condon approach would break down numerically. A method for treating the reaction which does not suffer from this breakdown was sketched in Reference 24.

In the case of highly exothermic or highly endothermic reactions, in contrast, the saddle-point lies in the entrance or exit

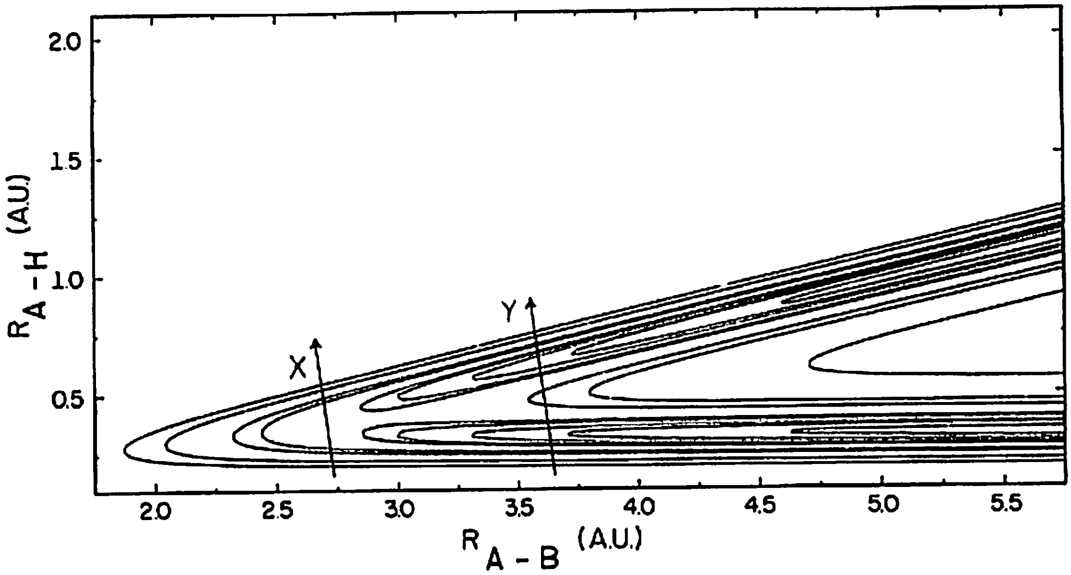

FIGURE 5. Skewed-axis plot (52) for a proton transfer reaction A-H$^+$ + B → A + B-H$^+$; R_{A-H} denotes a scaled A-H$^+$ distance, and R_{A-B} denotes a scaled distance between B and the center of mass of A-H$^+$. The lines give the potential energy contours, and the system moves from one valley to the other, either via the saddle-point (cf. line X) or before then (cf. line Y).

channels respectively, and there is no simple relation to electron transfer and to the Franck-Condon arguments used in electron transfer theory (51).

Proton transfers at the surface of the membranes can be treated in a way which bears some analogy to the treatments [(51) and references cited therein] of proton transfers at electrode surfaces, once the mechanism and rates of these biochemical proton transfers become identified.

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DISCUSSION

HOLSTEIN: Which of the two cases discussed in the H_2 + H reaction is related to the Franck-Condon principle? I would think that Franck-Condon is valid when the saddle point is classically accessible.

MARCUS: In the $H_2 + H \rightarrow H + H_2$ reaction, the bond length in the reactant gradually adjusts to the motion along the "reaction coordinate", as does that of the outgoing product. So for this reaction, the use of a first-order perturbation theory Franck-Condon approach is not appropriate. In a reaction of the type $MH + M' \rightarrow M + HM'$, where M is a relatively heavy group, e.g., as in most proton transfers in solution or as in many H-atom transfers in the gas phase, the case where the transfer occurs before the saddle-point region is reached is the case more amenable to a Franck-Condon approach, wherein one calculates the overlap of the MH and HM' vibrational wave functions. When instead, the reaction occurs by passage through the saddle-point region in the potential energy surfaces, where the MH and HM' channels have merged, the two bonds have adjusted themselves to motion along the reaction coordinate and use of a Franck-Condon approach to calculate the reaction rate again becomes inappropriate.

BRÖCKLEHURST: I would like to add to what Dr. Marcus has said about the need for studies between aromatics, that work is in progress - mostly by Michael Szwarz - on the radial ions of aromatic hydrocarbon atoms which are tied to gether by alkane chains.