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Light-Induced Charge Separation in Biology and Chemistry

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The conversion of solar light energy into other useful forms of energy is not only the basis of life on earth (photosynthesis), it is also one of the goals of present research for the development of new energy sources.

In this volume the energetics, kinetics, and structural prerequisites of the generation and separation of electric charge carriers are analyzed for various relevant examples in biology and technique. Experts of different fields discuss the problems of molecular mechanism, reaction rate, efficiency, structural organizations, and experimentation from their point of view. The degree of understanding and open questions are outlined in the group discussions. The result is a comprehensive survey of our present knowledge of this fundamental process.

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Electron Transfer and Tunneling in Chemical and Biological Systems

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Abstract. Various aspects of electron transfer reactions in chemical and biological systems are discussed. They include the role of potential energy surfaces, nuclear tunneling, temperature behavior, thermodynamic factors, relation of the preexponential factor in the rate constant to electron tunneling, the effect of applied electric fields, and charge transfer and other spectra. Classical and quantum equations are given, and the relation between recent and earlier quantum theories is discussed. Several biological reactions are considered with these results in mind, utilizing some information available in chemical systems.

INTRODUCTION

The present paper concerns a variety of aspects of electron transfer reactions listed in the abstract. We begin with a consideration of the relevant potential energy surfaces.

POTENTIAL ENERGY SURFACES AND MECHANISM

To treat rates of reactions in general, regardless of whether they involve transfers of electrons (47), atoms, or protons (23), bond scission, or molecular isomerization, it is useful to plot potential energy curves. The potential energy U is a function of the positions of all the atoms in the system. Thereby, U depends, for example, on all the bond lengths and angles, on orientations of reacting molecules, and on distances and orientations of molecules in the surrounding environment (47). Because there are so many position

coordinates involved, only a profile of U versus some general coordinate can be plotted, which has as components all of the coordinates above (47). Such a plot is useful for pictorial purposes, although the actual calculations themselves involve all instead of one general coordinate.

It is useful to classify electron transfer reactions as "normal" or "abnormal" according to the reactants' and products' U-curves in Fig. 1 or in Fig. 2, respectively.

The position of each atom in the entire system is subject to thermal fluctuations and the reactive system thereby wanders over the curve R (really surface R) in Fig. 1. In Fig. 1 no reaction occurs until the system reaches the coordinates at the intersection of the R and P surfaces. At that intersection, the system can go from the reactants' surface R to the products' surface P when there is a coupling between the orbitals of the two reactants (47). The extent of coupling of the two electronic orbitals (one on one reactant, occupied by the electron to be transferred, and an orbital on the other reactant, waiting to be occupied by the transferred electron) is reflected in the splitting 2ε of the intersecting R and P curves, as in Fig. 1.

The probability of reaching the intersection can be calculated by statistical mechanics or by some related formalism. The probability of the systems' crossing from the R to the P curve can be calculated by quantum mechanics with a velocity-weighted Landau-Zener (37,38,58,79,80) transition probability κ, cf. (50). The weaker the electronic coupling of electronic orbitals of the reactants with each other, the smaller is this κ. It has a maximum value of unity at strong coupling, at least in the case[1] shown in Fig. 1 (47). (Superscripts refer to footnotes in Appendix A.) The influence of a small ε on the R and P curves is, unlike Fig. 1, where a splitting is caused, not as evident pictorially as can be seen in Fig. 2.

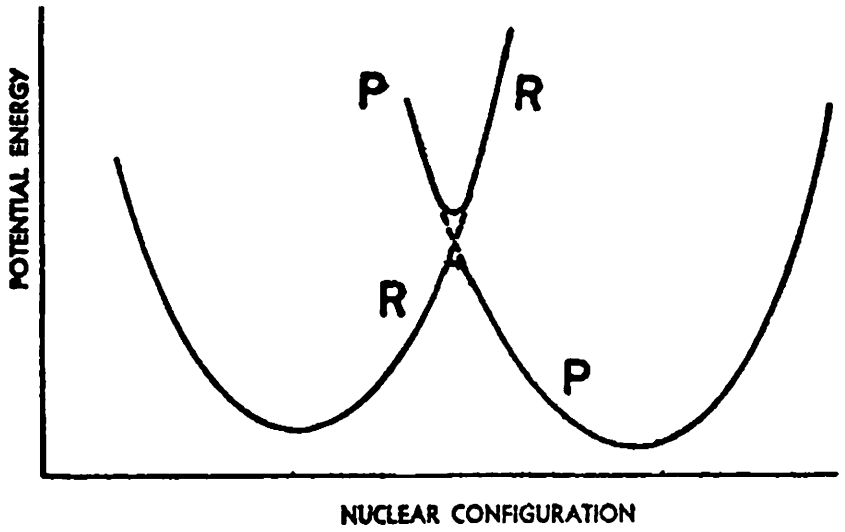

FIG. 1 - "Normal" electron transfer reaction. Profile of a plot of the potential energy of the system of reactants plus environment (R) and products plus environment (P) versus the configuration of the nuclei of the entire system. The plot is made for an approximately thermoneutral reaction, and (dotted lines) is made for the case of no electronic interaction between the reactants and (solid lines at intersection) for the case of finite electronic interaction.

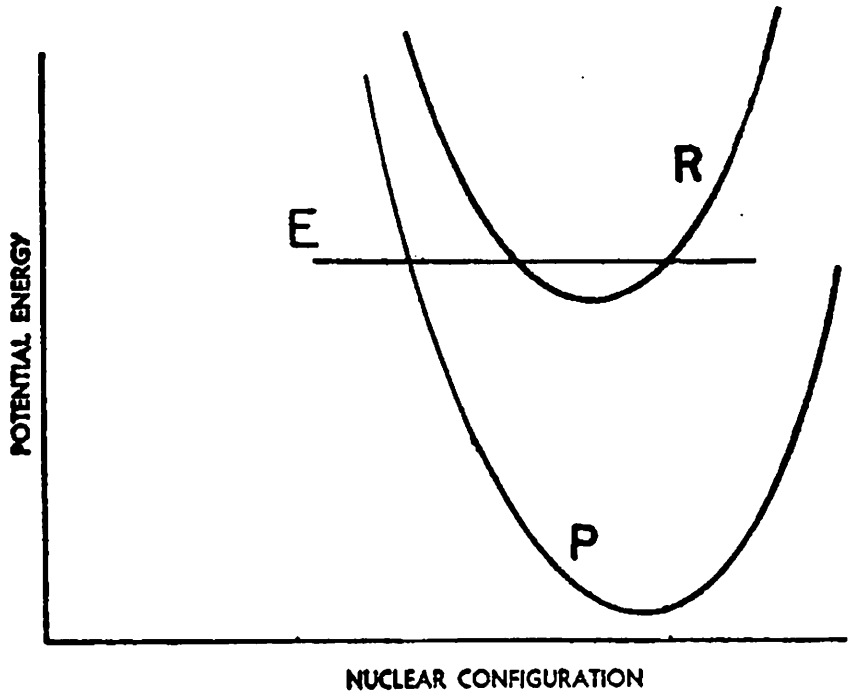

FIG. 2 - "Abnormal" electron transfer reaction. Same as in Fig. 1, but for a reaction where the R and P curves do not intersect at readily accessible thermal energies, i.e., for a very exothermic reaction.

NUCLEAR TUNNELING

At low enough temperatures the thermal fluctuations in the system are too small (reflected in a small Boltzmann factor) to permit the system to go over the top of the barrier in Fig. 1. Instead the system in one of its lower vibrational states tunnels through the potential energy barrier created by the R and P surfaces, as in Fig. 3.

In Fig. 2 when the two surfaces do not intersect at a thermally readily accessible region, or at all, nuclear tunneling could occur even at room temperature.

TEMPERATURE BEHAVIOR

The temperature behavior of the rate constant k_r is interesting. In the case illustrated in Fig. 1, a plot of ln k_r versus 1/T would have a finite slope at the higher temperatures and, because of nuclear tunneling, essentially zero slope at very low temperatures. At high temperatures there is no nuclear tunneling in the case of Fig. 1. At low temperatures the reaction proceeds exclusively by nuclear tunneling from the lowest vibrational state(s) of the reaching pair, and so is then temperature independent. At high temperatures the rate

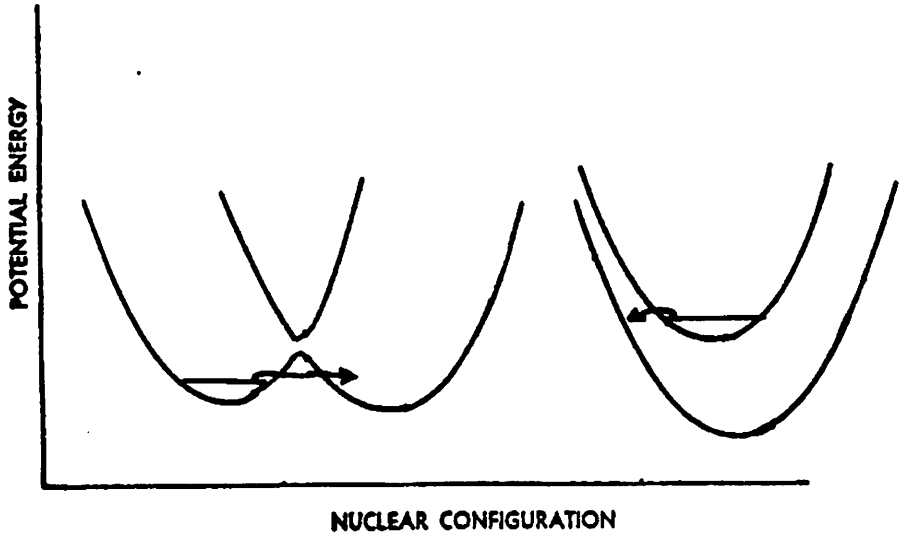

FIG. 3 - Nuclear tunneling through the barrier.

constant is of the form

$$k_r = A \exp(-E_a/kT) \quad , \qquad (1)$$

and the value of A can be of particular significance for electron tunneling, a point to which we return later.

Instead of the temperature behavior in the above example, ln k_r may be independent of 1/T, a result that could be due either to the intersection of the P curve in Fig. 1 with the R curve near the latter's minimum, or due instead to nonintersection as in Fig. 2. In the case shown in Fig. 2, an increase of mean thermal energy decreases the nuclear tunneling path length between the two curves and results in a higher nuclear tunneling rate. However, such a temperature effect on nuclear tunneling is usually assumed to be small. Thus, a situation in which ln k_r is essentially independent of temperature at all temperatures does not in itself imply nuclear tunneling - such behavior could be the result of nuclear tunneling in the case of Fig. 2, but not in the Fig. 1 case, where the P curve intersects the R curve at its minimum.

RELATION OF THESE POTENTIAL ENERGY SURFACES TO THERMODYNAMIC FACTORS

In any mechanism it is desirable to determine the rates of the individual reactions, when there are more than one, and Fig. 1 or 2 is intended to describe an individual electron transfer step in the overall reaction. To understand adequately the electron transfer step and the interpretation of its rate constant k_r, a knowledge of the thermodynamics for that reaction step is needed. The vertical distance between the minima of the R and P surfaces represents, approximately, the energy of reaction ΔE_r^o, under the prevailing conditions and at the separation distance r for electron transfer. The reaction is exothermic (and so ΔE^o is negative) when the minimum of the P curve is below that of the R curve (cf. Fig. 2). Another important thermodynamic property of the reaction is the (standard) entropy of reaction ΔS^o. The curves in Fig. 1 are depicted as parabolas for pictorial simplicity. However, when conformational changes or (because of the change in charge distribution)

reorientation of any polar molecules in the environment or electrostrictive effects occur, the shape of these curves can be very complicated and far from parabolic, when, say, the orientational coordinates change. ΔS^o describes the shape of energy surface P of the products in Figs. 1 and 2 relative to that of the reactants' R. For example, when the shape of the of the surface of the product near its minimum (minima) has a relatively small curvature in a thermally accessible region, while that of the reactants has high curvature in the thermally accessible region, the products (and environment) have much more freedom of movement than do reactants (and environment), and ΔS^o is quite positive. The converse is likewise true.

Factors influencing the reaction rates in addition to the thermodynamic quantities ΔE_r^o and ΔS^o are the transition probability κ and the horizontal displacement between the minima of the reactants' and products' curves. When this horizontal displacement is large, the two curves in Fig. 1 intersect only at high value of U. The horizontal displacement is related to the value of λ in Eq. 2 below. The displacements, horizontal and vertical, also affect the nuclear tunneling rate.

EQUATIONS: NO NUCLEAR TUNNELING

An equation widely used in the literature of electron transfer reactions is of the form (45),

$$k_r = B \exp[-\frac{\lambda}{4kT}(1 + \frac{\Delta}{\lambda})^2] \quad . \qquad (2)$$

We consider the values of B, λ and Δ, as well as the limitations of the equation. Some of the extensive applications have been described elsewhere (e.g., (2,7,42,49,52)), and the theory of electron transfer reactions has been reviewed recently (68,69).

The equation was first derived for bimolecular reactions in solution with a value of $\kappa \cong 1$ (quantum mechanically "adiabatic" (45). The derivation was later extended to reactions which were not adiabatic (e.g., $\kappa \ll 1$) (42,50), to first order

reactions (50), adiabatic or nonadiabatic, and to reactions at electrodes (46,50). It was noted that for highly exothermic reactions ($-\Delta > \lambda$), increasingly negative Δ decreased k_r instead of increasing it (47). (The "abnormal" region, Fig. 2, was termed "inverted behavior" in (47).)

The value of B in (50) depends on whether the reactants can move in the environment freely (bimolecular reaction) or whether they are bound together (termed here 'unimolecular'). For a bimolecular reaction, B is given by

$$B = \kappa Z \exp(-w^R/kT) \qquad \text{(bimolecular)} \qquad (3)$$

where κ is an electron tunneling factor; Z is about 10^{11} ℓ $mol^{-1}sec^{-1}$; w^R is the free energy (electrostatic, nonpolar, steric, conformational) to bring the reactants to the most favorable distance r for electron transfer. Modifications in k_r when encounter complexes occur are discussed in Appendix B.

For a unimolecular reaction there may or may not be a prior reorganizational (conformational) free energy required, which we shall denote by w^R. For the 'unimolecular' case,

$$B = \kappa\nu \exp(-w^R/kT) \qquad \text{(unimolecular)} \qquad (4)$$

where ν is about 10^{13} sec^{-1}.

In Eq. 2 λ is a quantity expressed in terms of bond force constants, changes in equilibrium bond lengths in each reactant, in sizes and changes in charge of each reactant, and the dielectric properties of the surrounding environment (47,50). The greater the horizontal displacement of the minima of the two curves in Figs. 1 and 2, the greater the value of λ. An expression λ in terms of molecular properties is given in (47,50).

Δ denotes the standard free energy of reaction at the distance r for electron transfer, ΔG_r^0:

$$\Delta = \Delta G_r^0 \quad . \qquad (5)$$

ΔG_r^0 can be expressed in terms of ΔG^0, the value at infinite separation, w^R and $-w^P$, the work to separate the products from r to ∞ (where w^R and w^P denote prior conformational terms in the unimolecular case).

$$\Delta G_r^0 = \Delta G^0 + w^P - w^R \quad . \tag{6}$$

Electrode reactions have also been treated similarly (11,25, 40,41,46,48,50).

Both w^R and λ are "reorganizational" terms, but one of them precedes the step controlled by the free energy change Δ. Only the free energy barrier created by the other (λ) can be affected by a favorable free energy change Δ.

The Landau-Zener transition probability, when velocity-weighted, yields[2] for $\kappa\nu$ in Eq. 4, in the limit of low κ,

$$\kappa\nu = (\pi/\lambda\ kT)^{1/2}\ (\varepsilon^2/\hbar) \qquad \text{(small } \kappa\text{; unimolecular)} \tag{7}$$

Eqs. 2-4 were first obtained by a classical mechanical argument (47,50). Use of the Landau-Zener κ as above then yields Eq. 7 for the case of $\kappa \ll 1$. Eqs. 2 and 7 have also been obtained from quantum mechanical arguments, by assuming the equivalent of $\kappa \ll 1$ and then proceeding to the classical limit of the quantum mechanical rate expression (40-42). In (40-42), the system is treated as a collection of harmonic oscillators, with frequencies for the products and environment assumed to be the same as those of the reactants and environment. For such reactions ΔS^o was assumed to be zero. Quantum mechanical first-order perturbation theory was used ("Golden Rule"), and Franck-Condon overlap integrals involving the vibrational wavefunctions of the reactants and products were calculated. In the high temperature limit Eq. 2 was obtained with B given by Eq. 7 and Δ given by Eq. 8 instead of Eq. 5:

$$\Delta = \Delta E_r^0 \quad . \tag{8}$$

Depending on the treatment, either the vibrational or the solvational or both parts of λ have been included. With Δ

given by Eq. 8 instead of Eq. 5, Eq. 2 of course no longer obeys microscopic reversibility, unless $\Delta S^0 = 0$.

The quantum mechanical theory provides not only the "high temperature" (classical) limiting behavior embodied in Eq. 2, but also the behavior at temperatures where nuclear tunneling occurs and so is of interest in describing the entire temperature range. It is considered in a later section.

Eq. 2 is based on the systems' reaching the intersection of the R and P curves in Figs. 1 or 2 and ceases to be appropriate when nuclear tunneling becomes important (unless one incorporates into κ a nuclear tunneling factor). In the case of Fig. 2, nuclear tunneling could be very important, and in the case of Fig. 1 it could be important at low temperatures. Instead of Eq. 2 one can obtain (when $-\Delta \gg \lambda$) an expression whose exponent varies much more slowly with Δ. It can depend linearly instead of quadratically on Δ, yielding the so-called "energy gap law" (26,72) for the rates of radiationless transitions.

Eqs. 2-4 in this paper apply regardless of whether a reactant is in the ground or in an electronically excited state. The quantities Δ and λ then refer to the reaction of this particular state with the one reactant. For example, if one compares the reaction of A^*_{red} with B_{ox} to form A_{ox} and B_{red} with A_{ox} unexcited,

$$A^*_{red} + B_{ox} \rightarrow A_{ox} + B_{red} \tag{9}$$

the Δ of this reaction will differ from that of

$$A_{red} + B_{ox} \rightarrow A_{ox} + B_{red} \tag{10}$$

by an amount that is essentially equal to the O→O transition energy for $A_{red} \rightarrow A^*_{red}$ (i.e., by an amount essentially equal to the electronic plus vibrational energy of A^*_{red} in its lowest vibrational state minus the corresponding quantities for A_{red}). The λ's of reactions 9 and 10 may also differ.

Eqs. 2, 3, 5, and 6 also apply to reactions at metal electrodes (46,50), but with $Z \cong 10^4$ cm sec^{-1} and with ΔG^o replaced by the electrochemical "driving force," $ne(E - E_o')$; here n is the number of electrons transferred and $E-E_0'$ is the half-cell potential relative to its value under "standard" conditions. The electrochemical λ is approximately one-half that for the corresponding self-exchange electron transfer reaction under certain conditions (46,50).

THEORETICAL VALUE OF A

The value of the pre-exponential factor A in Eq. 1 is given by

$$A = \kappa Z\, e^{\Delta S^*/kT} \qquad \text{(bimolecular)} \qquad (11)$$

$$A = \kappa \nu\, e^{\Delta S^*/kT} \qquad \text{(unimolecular)} \qquad (12)$$

where ΔS^* is a temperature derivative:

$$\Delta S^* = -(\partial/\partial T)[w^r + (\lambda/4)(1 + \Delta/\lambda)^2] \quad . \qquad (13)$$

Thus, when ΔS^* is either negligible or can be calculated, the measurement of A provides information on κ in the bimolecular and unimolecular cases.

EFFECT OF ELECTRIC FIELDS AND OF STANDARD FREE ENERGY OF REACTION ON REACTION RATE

We consider here the effects of varying the standard free energy and of varying an applied electric field on the reaction rate. The field can arise from other charges near the reactants (e.g., in or near the membrane when the reactants are in a membrane) as well as any externally applied field. When the potential energy curves are nearly nonintersecting in the very highly exothermic reaction as described in Fig. 2, an "energy gap law expression" should be applied instead of Eq. 2, if use of an approximate expression is desired. We consider the case of Fig. 1 first.

By adding different substituents to one of the reactants the standard free energy term ΔG_r^o can be varied when the

substituent affects the free energy of the oxidized form and the reduced form differently. Many experiments of this type have been undertaken. Under certain conditions the λ term is unaffected, namely, when the substituent does not affect the difference of equilibrium bond lengths of the two forms or the proximity of polar groups near the ionic charges. Under these conditions, introduction of a substituent merely raises or lowers the P curve in Fig. 1 relative to the R curve vertically, without displacing it laterally or changing the curvature of either curve (surface). When the variation in a substituent also leads to a change in λ, either or both of these additional changes in the curves in Fig. 1 would also occur. The influence of ΔG_r^0 on the rate constant is, in the case of Fig. 1, given by Eqs. 2 and 5 and has been extensively studied experimentally (52,73).

For the case of an applied electric field for a reaction between oxidized A and reduced B at a separation distance r

$$A_{red} + B_{ox} \rightarrow A_{ox} + B_{red} \quad \text{(distance r)} \tag{14}$$

we denote the charges of the reactants by e_A^R and e_B^R and those of the products by e_A^P and e_B^P. The applied field produces a potential ψ_A and ψ_B at the centers of charge of A and of B. The $\Delta G_r^0(\psi)$ equals the value at $\psi = 0$, $\Delta G_r^0(\psi = 0)$, plus an added contribution:

$$\Delta G_r^0(\psi) = \Delta G_r^0(\psi = 0) + \Delta e_A(\psi_A - \psi_B) \tag{15}$$

where Δe_A denotes $e_A^P - e_A^R$ and hence denotes $-(e_B^P - e_B^R)$. In turn, if the electric field vector is $\underset{\sim}{E}$ in this vicinity and if $\underset{\sim}{r}$ denotes a vector directed from the charge center of B to that of A, $\psi_A - \psi_B$ equals $-\underset{\sim}{E}\cdot\underset{\sim}{r}$ for the case of a locally constant field $\underset{\sim}{E}$.

The region of Δ, which defines the regime appropriate to Fig. 1, is $-\lambda < \Delta < \lambda$. In this regime the rate constant varies with $\Delta (= \Delta G_r^0)$ according to Eq. 2 as

$$kT \ \ell n \ k_r = \text{constant} + \frac{\lambda}{4} + \frac{\Delta}{2} + \frac{\Delta^2}{4\lambda} \quad . \tag{16}$$

The slope of a plot of $kT \ \ell n \ k_r$ versus Δ is

$$d \ kT \ \ell n \ k_r/d\Delta = \frac{1}{2} \ (1 + \Delta/\lambda) \quad . \tag{17}$$

Thus, this slope varies smoothly from a value of 0 at $\Delta = -\lambda$, through a value of 1/2 at $\Delta = 0$ and finally to a value of 1 at $\Delta = \lambda$, in the domain $-\lambda < \Delta < \lambda$ appropriate to Fig. 1. Thus, the applied field will have negligible effect on k_r in the vicinity of $\Delta = -\lambda$, an effect about equal to $1/2 \ \Delta e_A(\psi_A - \psi_B)$ in the vicinity of $\Delta = 0$ and an effect of about $\Delta e_A(\psi_A - \psi_B)$ in the case of a reaction that is very "uphill" ($\Delta \cong \lambda$).

Outside the domain ($-\Delta < \lambda < \Delta$) appropriate to Fig. 1, namely, when $\lambda < |\Delta|$, caution is needed in applying Eq. 2. Calculations by Eq. 18 below show that at high vibration frequencies $kT \ \ell n \ k_r$ is much less sensitive to changes in Δ than implied by Eq. 16 when the latter is applied in the range $\lambda < |\Delta|$. Thus, electric fields would then have relatively small effect in this region, much as they do in the case of Fig. 1 when $\Delta \cong -\lambda$.

The effect of electric fields on rates have been extensively studied in the case of electrode reactions at metal electrodes, e.g., (11,21,25,40,41,46,48,50), as already noted. For example, A in Eq. 15 is the reactant and B is the metal electrode. In that case $\psi_B - \psi_A$ is the potential difference between the electrode and the solution at the distance where A is undergoing electron transfer. The arguments have been extended to semiconductor electrodes (10,22,40).

CHARGE TRANSFER SPECTRA

Electron transfer can be assisted by light not only by producing electronically excited species, which then are reactive, as in Eq. 9, but also more directly: Absorption of light in the presence of sufficient electronic coupling between the reactants yields the vertical transition depicted in Fig. 4. This is a charge transfer transition.

These charge transfer spectra, or intervalence spectra as they are sometimes called, have been extensively studied (31,32). The intensity of the absorption band depends on factors such as the extent of electronic coupling of the electronic orbitals of the two reactants, and the intensity of the spectra has been used to estimate the splitting 2ε in Fig. 1 ((61), cf. (31,32)). If the splitting ε is too small, the intensity of the band can, of course, be too small to allow an adequate signal-to-noise ratio.

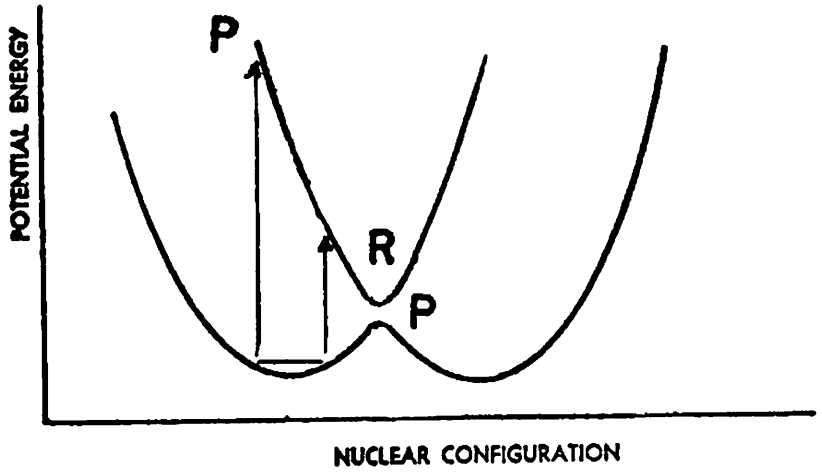

FIG. 4 - An electron transfer caused by light absorption in a single step. The vertical lines give a measure of the range of light frequencies absorbed.

Under favorable circumstances it would be possible to learn also about λ from charge transfer spectra in several ways: when the optical absorption of a metal ion reactant yields a charge transfer between the metal and the ligands in that reactant, the oxidation state of the metal is thereby changed. A comparison of the absorption and fluorescence spectra could then provide information on λ. If the fluorescence is from the electronic state formed in the absorption, a displacement (Stokes shift) between the long wave absorption maximum and short wave fluorescence maximum can be expressed (for small ε) in terms of the $0 \rightarrow 0$ energy and the contribution of that reactant to λ. At least it can be so

expressed in the absence of complications or when those complications are corrected for. Several cases involving tris-bipyridyl complexes of metal ions have been discussed recently (5,43) and compared (5) with λ contributions to the electron transfer rate.

Again, if at low temperatures the vibrational structure is resolved, information about λ can be further obtained. For example, assuming the dipole matrix element to be independent of the vibrational coordinates over the range of coordinates involved in the absorption (Condon approximation), then when the even transitions ($0 \rightarrow 0$, $0 \rightarrow 2$, $0 \rightarrow 4$, ...) of a symmetric vibration occurs, but not the odd ones ($0 \rightarrow 1$, $0 \rightarrow 3$, ...) in the optical change of electronic state, the surfaces, plotted versus that vibrational coordinate, are not horizontally displaced from each other. (Any antisymmetrical mode q has its minimum at $q = 0$ and so when plotted versus q the surfaces are not horizontally displaced.) The occurrence of $0 \rightarrow 2$, $0 \rightarrow 4$, ... transitions of a symmetric mode under such conditions arises from difference of vibration frequencies in the initial and final states, and so the intensities can provide a measure of those differences. Other spectral results for various aromatic molecules describe the displacement of the potential energy minima for the vibrational modes (55,56) (this example itself is not a charge transfer one, of course).

Large Stokes shifts occur when charge transfer occurs in a polar solvent (44,51,59) because of interactions with the polar environment, and so they should not be used when only the vibrational contribution is needed for application to a system in a nonpolar environment.

EQUATIONS. INCLUSION OF NUCLEAR TUNNELING

Eq. 2 does not include quantum effects associated with nuclear tunneling. While such neglect appears to be appropriate for most electron transfer reactions, Eq. 2 clearly does not apply when tunneling becomes important.

A quantum expression for the rate constant of electron transfers was given by Levich and Dogonadze (Eq. 43 of (42) or Eq. 10.2 of (40)) many years ago for the case of (a) very small electronic interaction (nonadiabatic electron transfer), (b) treatment of the polar solvent medium via a Fourier series as a collection of harmonic oscillators, all of frequency ν, and (c) frequencies unchanged by the reaction. Although condition (b) limits its application to biological systems, exactly the same equations arise, regardless of whether the oscillators are oscillators of the solvent or of the reactants.

For an exothermic ($\Delta < 0$) first order reaction one has (40, 42)

$$k_r = \kappa' \nu \; I_p(a/\sinh \gamma) \; \exp(-\frac{\Delta}{2kT} - a \coth \gamma) \quad . \qquad (18)$$

(The rate for the reverse endothermic reaction is Eq. 18 multiplied by $\exp(\Delta/kT)$.) In Eq. 18 I_p is the modified Bessel function and

$$p = -\Delta/h\nu, \quad a = \lambda/h\nu, \quad \gamma = h\nu/2kT, \quad \kappa' = (\varepsilon/\hbar\nu)^2 \quad . \qquad (19)$$

The factor in Eq. 18 multiplying $\kappa'\nu$ arises from a sum of Franck-Condon integrals for overlap of the reactants' with the products' vibrational wavefunctions, a sum over all final and (Boltzmann-weighted) initial states. Jortner has also obtained Eq. 18, namely, Eq. 4 of (33).[3] κ' defined by Eq. 19 can be termed the "nonadiabaticity factor," prompted by the result in Eq. 22 below, at $0^{\circ}K$.

Eq. 18 has been extended to systems with more than one frequency and/or to oscillators which are both displaced and distorted (i.e., frequency differences between reactants and products), e.g., (12,13,16,17,30,33,34,75,76) (cf. (26,72) for relevant Franck-Condon factors). Instead of Eq. 18 a semiclassical equation has been used by Hopfield (28,29) (cf. (18, 39,70)), written for brevity in the form of a single frequency:[4]

$$k_r = B' \exp[-(\Delta + \lambda)^2/2\lambda h\nu \coth (h\nu/2kT)] \qquad (20)$$

where

$$B' = \nu(\varepsilon/\hbar\nu)^2 [1/2\pi a \coth (h\nu/2kT)]^{1/2} \quad . \qquad (21)$$

In the classical limit ($\hbar \to 0$), Eqs. 18 and 20 both yield Eq. 2, with B equal to the $\kappa\nu$ in Eq. 7 and Δ being given by Eq. 8 (58).

Jortner (33) has shown that Eqs. 18 and 20 can differ numerically by several orders of magnitude at low temperatures, for the case p = 0. The limiting behavior at low temperatures is therefore of particular interest. At low temperatures (Eq. 10.6 of (40)) one has (33)

$$k_r = \nu(\varepsilon/\hbar\nu)^2 e^{-a} a^p/p! \quad . \qquad (22)$$

The coefficient of $\nu(\varepsilon/\hbar\nu)^2$ in Eq. 22 is the well-known (26, 72) Franck-Condon factor for the overlap of the lowest vibrational wavefunction of one electronic state with the p'th vibrational wavefunction of another. By comparison Eq. 20 yields

$$k_r = \nu(\varepsilon/\hbar\nu)^2 (1/2\pi a)^{1/2} e^{-(p-a)^2/2a} \quad . \qquad (23)$$

The coefficients of $\nu(\varepsilon/\hbar\nu)^2$ in Eqs. 22 and 23 differ by being normalized Poisson and Gaussian functions, respectively, in a (hypothetical) distribution of p. (The distribution is hypothetical since there is only one p, namely, $-\Delta/h\nu$.) The two will be approximately equal numerically, therefore, when both p (i.e., $-\Delta/h\nu$) and the "mean" value of p in the "distribution," namely, $\underline{a}$ (i.e., $\lambda/h\nu$) are both large. Large $\lambda/h\nu$ is the so-called "strong coupling" regime.

Eqs. 18 and 20 can differ greatly when ν is large: A plot of $\ell n\, k_r$ versus Δ gives a parabolic curve in the case of Eqs. 2 and 20. For large ν the curve is strongly asymmetric in the case of Eq. 18, being ultimately only linearly dependent on Δ when $-\Delta \gg \lambda$ (energy gap law).

In the case of very exothermic reactions, care is needed in using all of these equations, particularly in the case of Fig. 2. Significant errors due to anharmonic effects can arise when $|\Delta| \gg \lambda$ and can considerably influence the nuclear tunneling, or in Fig. 1 when the contribution of one reactant to λ is negligible relative to that of the other (preventing compensation effects (75)). In radiationless transitions, for example, anharmonic effects can lead to errors of orders of magnitude (26,72).

Finally, in cases where ϵ is large enough for the perturbation theory to break down, Eqs. 18 and 20 need modification of course.

BIOLOGICAL SYSTEMS

The sequence of reactions which we shall briefly consider in the case of bacterial photosynthesis are the following (cf. (15,53)), beginning with the reaction of the electronically excited bacteriochlorophyll dimer $BChl_2^*$:

$$BChl_2^* + BPh \rightarrow BChl_2^+ + PBh^- \quad (24)$$

$$BChl_2^+ + BPh^- \rightarrow BChl_2^{*T} + BPh \quad (25)$$

$$\text{and/or} \rightarrow BChl_2 + BPh \quad (26)$$

$$BPh^- + QFe \rightarrow BPh + Q^-Fe \quad (27)$$

$$\text{cyt } c^{II} + BChl_2^+ \rightarrow \text{cyt } c^{III} + BChl_2 \quad (28)$$

where BPh and Q denote a bacteriopheophytin and a quinone molecule, and T denotes a triplet state.

In the case of electron transfer between aromatic species (4) as well as between iron phenanthroline species (6,78), the fast rates of homogeneous electron transfers show that the λ is about 0.5 eV in (4) and about 0.4 eV in (6,78). These studies, made in polar solvents, also suggest that the major contribution to λ is actually from the reorientation of polar solvent molecules, with negligible contribution from the vibration of the reactants. Correspondingly, one would expect the

vibrational λ contribution from BPh to be very small in the membrane, BPh being also an aromatic (porphyrin) system. The $BChl_2$ may have a somewhat larger vibrational contribution to λ due to some looseness in the binding of one BChl to the Mg^{+2} of the other, and the possibilities thereby of some geometrical reorganization on loss of an electron. Interestingly enough, the Stokes shift for $BChl_2$ is appreciable: the absorption and fluorescence spectra have maxima at 863 and 902 nm, respectively (8), whereas for the monomer BChl (67) (and hence presumably for BPH) the Stokes shift is only a few nm. This appreciable difference presumably reflects the greater sensitivity of the dimer to some geometrical change upon change of electronic configuration (here, excitation).

In the case of quinones (57), electron transfer rates in a polar solvent again reveal a relatively small λ, about 0.7 volts. It again appears to be due largely to reorganization of the polar solvent, with presumably relatively little vibrational contribution (57). The presence in reaction 27 of a Fe quinone linkage may contribute to the latter's vibrational λ, because of the possibilities it offers for geometrical changes (Fe-O displacements) on charge transfer.

If the dielectric constant of the membrane is about 5 one expects the environmental contribution to be roughly one-half that in highly polar solvents, (cf. Eq. 4.33 of (47); m there equals -0.5 for a self-exchange reaction). On this basis one expects the environmental contribution to λ to be about 0.2 to 0.3 volts in the membrane. The fast hopping mechanism for conduction in aromatic crystals is an indication of a relatively small vibrational λ for aromatic systems.

The λ for the cytochrome c self-exchange is somewhat uncertain. It is not yet definitely known whether the activation energy in the self-exchange (54,74) is due to a λ for this system or to a conformational w^R. (The looseness of the binding in the fifth and sixth positions of the heme could contribute to λ. I am indebted to N. Sutin and H. Gray for very helpful discussions of these and related questions.)

Thermodynamic data, such as the Δ for individual steps in reactions 24-28, are becoming available. The mid-point potential of the $BChl_2^+$-$BChl_2$ couple for Rps. sphaeroides is about 0.45 volts (36,60). From the average of the absorption and fluorescence maxima for $BCl_2 \rightarrow BChl_2^*$ (1.44 and 1.38 volts with an average of 1.41 volts) (8), the mid-point potential for $BChl_2^+$-$BChl_2^*$ is about -(1.41-0.45), i.e., -0.96 volts. The mid-point potential of the BPh-BPh^- couple is about -0.4 volts (in vivo value for Rps. viridis (63,64)·5, a contested value however. It may be about -0.6 volts (35).) With -0.4 volts, reaction 24 would be downhill by about 0.56 volts, and reaction 26 would be 0.45-(-0.4) or 0.84 volts downhill. The mid-point potential of the QFe-Q^-Fe couple is about -0.18 volts (62), so that reaction 27 is (0.4-0.18) or 0.22 volts downhill. The mid-point of the low potential cyt c in reaction 28 is about 0 volts, e.g., (14), so that reaction 26 is about 0.45 volts downhill.

Reaction 24 has a half-time of $\sim$10 psec (these and other data are given in (15)), and perhaps even as small as 3 psec; reaction 27 has a half-time of the order of 150 psec, and both reactions are temperature independent (1). The half-time for reactions 25 and 26 is of the order of 10 ns, the former being in the hyperfine coupling mechanism range (3,24,27,72). Reaction 28 is the slowest of all, about 1 μsec half-time in Chromatium for reaction with a low potential cytochrome (9,71).

The speed of reactions 24 and 27 is due to their small λ. If we assume an environmental contribution to λ of about 0.2 to 0.3 volt, for the reason discussed above, and a small effective vibrational contribution of say 0.2 volts for reaction 27, the net λ is 0.5 volts. The exponential factor in Eq. 2 then yields results "consistent" with the rates of reactions 24, 26 and 27 (κ' not yet known). If one assumes an environmental ν of the order of 300 cm^{-1}, $h\nu/2kT$ at room temperature is 0.725, $(h\nu/2kT)$ coth $(h\nu/2kT)$ is 1.17, and so Eq. 20 gives essentially the same results as Eq. 2 for the environmental contribution to the barrier for these reactions. Since $\lambda/h\nu$ is

large (about 13) and $-\Delta/h\nu$ for these reactions is also large, Eq. 18 also gives essentially the same result as Eqs. 2 and 20. Only when a large ν is used does Eq. 2 deviate from Eqs. 18 or 20 at room temperature; when $\lambda/h\nu$ is no longer large Eq. 20 deviates from Eq. 18. (Indeed many theoretical calculations are concerned precisely with the domain where $\lambda/h\nu$ is no longer large, e.g., (16,17,75), as revealed in their non-parabolic dependence of $\ell n\ k_r$ on Δ in the exothermic region $-\Delta > \lambda$.) A more accurate discussion would include the appropriate ν's for both the environmental and the vibrational λ's, and such calculations can readily be made, extending Eqs. 18 and 20.

Reaction 28, the slowest of all, is the best candidate for a small κ, because of a large separation distance (28,29) (cf. discussion sections of the volume in (53)). The latest experimental A in Eq. 1 for that reaction (cited in (53)) is about $5 \times 10^9\ sec^{-1}$. Thus, unless there is a ΔS^*, κ is of the order of 10^{-3}, an appreciable nonadiabaticity.

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APPENDIX A: FOOTNOTES

1. In the case of Fig. 2, if the R and P surfaces intersect, one can show that when the energy in this plotted coordinate exceeds the potential energy of the intersection, the probability of transition from the R to the P surface, per double passage past that point, passes through a maximum as a function of ε, being zero for small and large ε. In In the case of Fig. 1 the probability of transition at the intersection increases with increasing ε.
2. One uses Eq. 25 of (49), evaluates the slopes of the parabolas at the intersection and notes that there are two passages of the intersection point when κ is small, per "excursion" in the vicinity of that point, so that Eq. 25 is to be multiplied by 2.

In the denominator of Eq. 32 in (50) a one-dimensional configurational partition function $(kT/2\pi m^* \nu^1)^{1/2}$ was inadvertently omitted. I am indebted to Dr. DeVault on this point.

3. The p, λ, Δ, and ν in the present notation are the same as the p, $S\hbar\langle\omega_s\rangle$, $-\Delta E$ and $\langle\omega_s\rangle/2\pi$ of (33) and as the $|m|$, $z\hbar\omega_0 \sinh(\hbar\omega_0/2kT)$, J_2-J and $\omega_0/2\pi$ of (40). One notes that the z and V_{ab} of (40) are the same as $2S[\bar{\nu}(\bar{\nu}+1)]^{1/2}$, and $L_{21}^{(2)}$ of (33) and, as a little manipulation shows, the $[(\bar{\nu}+1)\bar{\nu}]^{p/2}$ and $S(2\bar{\nu}+1)$ of (33) are the same as the $\exp(-\hbar\omega_0/2kT)$ and the z $\cosh(\hbar\omega_0/2kT)$ of (40).
4. Hopfield's Δ is our λ.
5. Using the mid-point potential of BPh-BPh^- in Rps. viridis for that in Rps. spheroides is an assumption: the first contains bacteriochlorophyll b, while the second contains bacteriochlorophyll a.

APPENDIX B: ENCOUNTER COMPLEXES

If encounter complexes are formed, the overall rate constant k_r is given by a somewhat more complicated expression than Eq. 2. The electron transfer reaction of A_{red} with B_{ox}, written now in several steps, is

$$A_{red} + B_{ox} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (A_{red}, B_{ox}) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (A_{ox}, B_{red}) \xrightarrow{k_3} A_{ox} + B_{red} \quad . \tag{B1}$$

The two encounter complexes are those in parentheses, with an electron transfer step with rate constants k_2 and k_{-2}. Writing expressions for $(d/dt)(A_{red}, B_{ox})$ and $(d/dt)(A_{ox}, B_{red})$, setting them equal to zero (steady state approximation), and noting that the overall reaction rate is $k_3(A_{ox}, B_{red})$, one obtains Eq. B2 for the overall rate constant k_r instead of Eq. 2.

$$\frac{1}{k_r} = \frac{1}{k_{enc}} + \frac{1}{k_{act}\gamma} \quad , \tag{B2}$$

where k_{enc} is k_1, the rate constant for the formation of encounter complex (A_{red},B_{ox}), γ is the probability that the fate of (A_{ox},B_{red}) is to undergo electron transfer, $[\gamma = k_3/(k_{-2} + k_3)]$, and k_{act} is the activation-controlled rate constant (k_{act} equals k_2 times an equilibrium constant k_1/k_{-1} for the first step in Eq. B1). k_{act} is given by Eq. 2 of the text or, in the case of nuclear tunneling, by the later modifications in the text. Eq. B2 reduces to $k_r = k_{enc}$ or $k_r = k_{act}\gamma$, accordingly as $k_{enc} \ll k_{act}\gamma$ or $k_{enc} \gg k_{act}\gamma$, respectively.

When the rate of formation of (A_{red},B_{ox}) is diffusion-controlled, k_{enc} equals the well-known rate constant for a diffusion-controlled reaction (p. 129 of (47)),

$$k_{enc} = k_{diff} \quad . \tag{B3}$$

When the rate of formation of the encounter complex (A_{red}, B_{ox}) is activation-controlled instead of diffusion-controlled, due, for example, to a substantial reorganization of the solvent structure to form an encounter complex, k_{enc} can be

$$k_{enc} = Z \exp(-w_1^R/kT) \tag{B4}$$

instead of Eq. B3; w_1^R is the free energy barrier for forming this encounter complex from the reactants and equals w^R when the complex has no stability.

The particular case that $\gamma = 1$ and $k_{enc} = k_{diff}$ was discussed earlier (Eq. 6.1 of (52)).

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