SOME RECENT DEVELOPMENTS IN ELECTRON TRANSFER: CHARGE SEPARATION, LONG DISTANCES, SOLVENT DYNAMICS, AND FREE ENERGY ASPECTS

R. A. Marcus
Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91125
United States

ABSTRACT. Several topics in electron transfers are discussed, including the charge separation in a bacterial photosynthetic reaction center, long range electron transfers, solvent dynamical effects in electron transfer, and free energy aspects of these reactions.

1. INTRODUCTION

Studies in electron transfers now include a wide range of topics. In the present paper several of these are considered: (i) the high efficiency and rates for the photo-induced charge separation in the early reaction steps in bacterial photosynthesis, (ii) long range electron transfers, (iii) solvent dynamics in intramolecular and other electron transfers, and (iv) free energy aspects of these reactions. Extensive references to the relevant literature have been given in Refs. 1-4.

We first recall that an expression for an electron transfer rate constant k_e is given by[1]

$$k_e = A\, exp\,(-\Delta G^*/RT)\,, \tag{1a}$$

where the free energy barrier of reaction ΔG^* is

$$\Delta G^* = (\lambda + \Delta G^\circ)^2 / 4\lambda \tag{1b}$$

and where any work terms in the bimolecular case have been omitted from eq. 1b for notational brevity. The value of A in eq. 1a depends on whether the reaction is intramolecular or bimolecular, and whether it is adiabatic, nonadiabatic or inbetween;[1] λ is the sum of a vibrational λ_i and of an environmental λ_o (e.g., solvent or protein) term, $\lambda = \lambda_i + \lambda_o$, and is expressible in terms of the various properties of the reactants and of the medium; ΔG° is the "standard" free energy of the reaction step in the prevailing medium. When $\Delta G^\circ \simeq -\lambda$, the reaction becomes barrierless,

V. Balzani (ed.), Supramolecular Photochemistry, 45–52.

while when $-\Delta G^\circ \gg \lambda$ the reaction is said to be in the inverted region.[1] In the unusual situation where the motion of the dielectric becomes very sluggish the rate constant can depend not only on k_e but also on a dielectric relaxation time, as discussed in Sec. 3.

2. PHOTOSYNTHETIC CHARGE TRANSFER

The photosynthetic charge transfer system is remarkably efficient. Once the special bacterial chlorophyll pair $(BChl)_2$ receives its electronic excitation from the antenna chlorophylls, it transfers its electron to a pheophytin BPh some 9-10Å away (edge-to-edge distance)[5] in the strikingly short time of 2.8 picoseconds.[6a] The electron then transfers from the BPh^- to a quinone Q in the next 200 picoseconds. The back electron transfer to $BChl_2^+$ from Q^- or BPh^- is relatively slow.[6] Thus, nature has succeeded in setting up a rapid and efficient charge separation across the membrane containing this composite system.

This behavior has been the subject of many experiments and discussions.[6] One of the questions which arise concern the role played by a nearby bacteriochlorophyll molecule BChl. This molecule does not quite lie between the special pair $BChl_2$ and the pheophytin BPh, but it is close. The structures and the various distances involved are now known from recent crystallographic studies.[7] A second question which arises concerns the slowness of the back electron transfer from the BPh^- *to* the $BChl_2^+$, which, were it rapid, would destroy the possibility of an efficient charge separation. We consider both of these next.

2.1. Role of BChl in the charge separation

There are several possibilities for the role of the monomeric BChl in the charge separation: it may serve as a bridge for the electron transfer from the special pair to the pheophytin (superexchange mechanism) or serve, instead, as an actual intermediate $BChl^-$. We discussed these possibilities in a recent article.[2] Magnetic field data show that the interaction between $BChl_2^+$ and BPh^- is extremely weak (~10 G), a weak interaction which is in marked contrast to the fast rate of electron transfer from the excited $BChl_2^*$ to BPh[2]. We estimated in Ref. 2 that the resulting superexchange mechanism for a transfer from $BChl_2^*$ to BPh via the BChl was too slow by a large factor, perhaps as much as 1000, to account for the experimentally observed fast rate of loss of an electron from $BChl_2^*$. A mechanism involving $BChl^-$ as an intermediate appears, instead and thus far, to be consistent with the data.[2] Detection of $BChl^-$ itself would be desirable, but the detectability depends on the relative rate constants for formation and destruction of $BChl^-$. This point was further discussed in Ref. 3. A third possibility is the direct transfer from $BChl_2^*$ to BPh, i.e., no role for the BChl. In virtue of the distances involved, considered later in Sec. 3 together with available data on the distance dependence of long range electron transfers, this third possibility can, we believe, be ruled out, because the observed electron transfer rate is so high (Sec. 3).

2.2. Role of the high $-\Delta G°$ of the back reaction

The extreme rapidity of forming BPh^- by electron transfer from $BChl_2^*$, even though the driving force, the $-\Delta G°$, of this reaction appears to be relatively small, indicates (via eq. 1) that the reorganization term λ for the reaction is also small, both for $BChl_2^* \rightarrow BChl$ and the $BChl \rightarrow BPh$ electron transfers.[2] It may be ~0.1 to ~0.2 eV. On the other hand, the driving force for a back reaction from BPh^- to reform a ground state $BChl_2$ molecule is large (~1.2 eV),[5] thus placing this reaction very much in the "inverted" region and hence reducing its rate;[1] indeed, it would be so deep in the inverted region that quantum vibrational effects could well be important and eq. 1b would be replaced by the appropriate quantum expression.[1]

Since reformation of an excited singlet $BChl_2^*$ in the back reaction may be somewhat uphill, in terms of free energy, and since re-reaction (~3 ps) is much faster than fluorescence (nanoseconds), this second possible path for electron transfer from BPh^- also does not effectively compete with electron transfer from BPh^- to Q (~200 ps). The remaining avenue for the back reaction is the formation of a triplet state $BChl_2^{*T}$, but it, too, because of the need for spin interconversion requires nanoseconds.[6a]

The environment of these pigments $BChl_2$, BChl and BPh is largely hydrophobic,[7] leading to only a small environmental λ_o. The structures of the relevant reactants (porphyrin bases or porphyrin complexes with Mg^{2+}) presumably lead to a small vibrational λ_i, since λ itself is small. A small vibrational λ_i would be due, in part, to the porphyrin rings not undergoing significant changes in bond lengths upon gaining or losing an electron, the rings themselves being large, and to any metal-ligand bonds not undergoing any significant changes in bond length: the Mg in the $BChl_2$ and BChl remains in the same oxidation state Mg^{2+} throughout.

This small λ, coupled with the large negative $\Delta G°$ for the back reaction, places that reaction in the "inverted region", we have concluded above, and so provides a barrier to this potentially best path for this unwanted back reaction.

In summary, the main ingredients in this efficient nature-made charge separation system appear to be, in the initial steps, reactants which have a small λ (hydrophobic environment, no major changes in metal-ligand bond lengths or in the bond lengths in the large ligands themselves), plus several slightly downhill steps across the membrane, followed by a more downhill one forming a distant semiquinone Q^-.

3. LONG RANGE ELECTRON TRANSFER

Information on long range electron transfer is now becoming available from several sources. These include the work of Miller and coworkers, and of Khairutdinov *et al.*, in frozen glasses and the work of Kuhn and coworkers and others on conduction through surface monolayers (and multilayers).[8] A typical exponent β for the dependence of electron transfer rate on distance ($\sim \exp[-\beta r]$) is about 1.1 $Å^{-1}$.[8] The literature was surveyed in 1985.[1] Since then, information has become available from additional

sources. Preliminary measurements by Gray *et al.* of long-range electron transfer between an electronically-excited zinc porphyrin ZnP^*T and various singly ruthenated (Ru^{3+}) proteins consisting of zinc-iron hybrid myoglobin, indicate a β of about 1 to 1.4 $Å^{-1}$.[9] The edge-to-edge distances involved varied from 14.5 to 22 Å.[9]

Intramolecular electron transfer has been studied by Hush, Paddon-Row, Verhoeven and coworkers[10,11] for a series of molecules whose pair of reactants are separated by rigid saturated hydrocarbon bridges of various lengths. In one study the latter was varied from 11.4 to 14.9 Å in direct straight line distances.[11] From these data, I estimate a β of somewhere between 1.2 and 1.4 $Å^{-1}$. Because of the curved nature of these bridges,[11] it is not clear whether this transfer itself is through the solvent medium or "through bond". Regardless, an interesting feature of the results is that this saturated hydrocarbon bridge does not provide a path for electron transfer easier than the intervening solvent molecules in the experiments of Miller and others; β is about the same. Work by Isied *et al.*[12] on an $Os^{II}-(isoproline)_n-Co^{III}$ system indicated a β of about 2 $Å^{-1}$. The exponent β is expected to depend somewhat on the system, and this dependence has been studied.[13]

With information on β thereby available from a variety of sources we can now consider the possibility of a direct transfer from the $BChl_2^*$ to BPh in Sec. 2, rather than the indirect one via BChl. The reaction is barrierless and so, as we have noted elsewhere,[1,2] an approximate nonadiabatic expression for the rate is readily deduced. The ratio of the rate constants under these conditions is $\exp(-\beta\Delta r)$, where Δr is the difference of edge-to-edge distances for the $BChl_2-BChl$ and the $BChl_2-BPh$ pairs, namely about 5 Å.[5] Using a β of 1.1 $Å^{-1}$ the rate constant of the direct transfer to BPh is expected to be about $\exp(-6.6)$ or about a factor of 10^{-3} slower than that occurring via the BChl. The reaction time estimated for the $BChl_2^*$ to BChl transfer, using the magnetic data for the interactions, was close to the observed value.[2] Thus, a direct transfer from $BChl_2^*$ to BPh is much too slow to account for the observed rate of electron transfer from $BChl_2^*$.[2]

By having, thereby, a series of intermediate sites between the $BChl_2^*$ and the quinone Q, and a small λ for the initial steps, $BChl_2^* \rightarrow BChl \rightarrow BPh$, the charge separation across the membrane can occur rapidly. The uphill reformation of $BChl_2^*$, the spin-restricted reformation of $BChl_2^{*T}$, and the excessively downhill reformation of $BChl_2$ are each relatively slow.

4. SOLVENT DYNAMICS AND ELECTRON TRANSFER

The rates of electron transfer in typical solvents and for typical reactions are largely dominated by the free energy barrier (eq. 1) arising from the reorganization of the environment (solvent or, in the case of reactions in a protein, the protein itself) and from any changes in bond lengths or angles of the reactants.[1] However, under some circumstances the sluggishness of the solvent motion itself can play a role, and there is some recent experimental evidence for this in several cases, as in the work of Huppert and Kosower, Clark *et al.*, and others.[14]

When the vibrational contribution λ_i to λ is negligible the reaction coordinate involves purely the motion of the solvent molecules themselves. There are viscous and "inertial" aspects to this solvent motion and under appropriate circumstances they affect the rate constant.[3,4,14] When the free energy barrier (the ΔG^* in eq. 1) is negligible, and when the vibrational λ_i is also negligible relative to the solvational λ_o, the reciprocal of the rate constant is predicted to approximately equal the "constant charge" dielectric relaxation time τ_L of the solvent.[3,4,14] Indeed, this behavior is now known to occur in a number of studies of photoinduced intramolecular charge transfers in polar solvents.[14]

More generally, when $\lambda_i = \Delta G^* = 0$, the reciprocal of the electron transfer rate constant is given approximately by τ:[15]

$$\tau \simeq k_e^{-1} + \tau_L \qquad (\lambda_i = \Delta G^* = 0) \tag{2a}$$

which reduces to k_e (eq. 1) when $k_e << \tau_L^{-1}$, and to τ_L when $\tau_L^{-1} << k_e$. The reaction coordinate contributing to the A in eq. 1, when $\lambda_i = 0$, involves the inertial motion of the solvent dielectric polarization (for reactants fixed in position).

When λ_i is small but not entirely negligible we have, instead,[3a,b]

$$\tau \simeq k_e^{-1} + F\tau_L \tag{2b}$$

where F is a known function of the $\Delta G^*/RT$ in eq. 1 and of λ_i/λ_o,[3] the ratio of vibrational to solvational contributions to λ.

At large τ_L, however, we found that in the case of a non-negligible λ_i a new behavior[4]: Instead of eq. 2, which for large enough τ_L yields $\tau \propto \tau_L$, we obtained[4]

$$\tau = C\tau_L^{\alpha} \qquad (\text{large } \tau_L, \lambda_i \neq 0) \tag{3}$$

where α is some constant between 0 and 1; α approaches 1 when $\lambda_i/\lambda_o \to 0$ and approaches 0 when $\lambda_i/\lambda_o \to 1$. C is a constant known, as was α, from a numerical solution of the relevant reaction-polarization diffusion differential equation.[4]

The field of solvent dynamics is predicted to display a richness in another respect also. In a purely activation-controlled, i.e., a k_e controlled electron transfer reaction, the survival probability of a reactant should decay exponentally with time, when the electron transfer is intramolecular or when it occurs bimolecularly but between reactants fixed in position. However, when τ_L becomes large and λ_i / λ_o becomes non-negligible strong deviations from this single-exponential behavior are predicted.[4] Another source of unusual time behavior can occur when there are significant deviations from the Debye relaxation behavior.[16]

The question naturally arises whether any of these results on solvent dynamics are relevant to electron transfers in protein systems. I am not aware of any evidence, thus far, which requires the invoking of a slow

"solvent" dynamics for the early forward steps of the photosynthetic system discussed earlier. Some conformational changes may arise in a back reaction from Q^- (this has been inferred indirectly[17] from a complicated temperature dependence of delayed fluorescence in samples containing Q^-). It may happen, too, that such changes are better treated by a kinetic scheme than by a "diffusive" (viscous) one.

5. FREE ENERGY ASPECTS

One key question which has been of interest involves the role of energy versus free energy in the theoretical rate expressions. For example, in two expressions which have been employed for the rate of a nonadiabatic reaction in recent years a classical treatment of the solvent polarization and a quantum treatment of the vibrational motion have been used.[18,19]. The starting point in these derivations was the "Golden Rule" for a radiationless transition, such as an electron transfer chemical reaction. One expression[18] contains the energy of reaction rather than free energy of reaction in the exponential (eq. 15 in Ref. 1). Such an expression is, however, typically restricted to reactions for which there is zero entropy of reaction, $\Delta S°$ and does not provide a good description of the ion-solvent interactions. A more general expression, which involves the free energy, has also been used (eq. 16 in Ref. 1).[19] Recently, it was derived from the same Golden Rule starting point.[20] By introducing general WKB rather than harmonic oscillator expressions for the solvent wavefunctions, the assumption of $\Delta S° = 0$ was avoided and the more general expression obtained.[20]

A second aspect of this free energy description is also of interest. Usually, in discussions of electron transfer reactions two intersecting parabolic curves are drawn, one for the reactants plus environment and one for the products.[1] These profiles of the two potential energy surfaces are introduced only for purposes of discussing the mechanism and are intended to be purely pictorial. The two actual potential energy surfaces used in the theory, when plotted along some of the coordinate axes - those describing the orientational coordinates of the polar solvent molecules - are much more complicated. (The vibrational potential energy function is nearly a quadratic, though.)What has been assumed in the theory for the solvent motion[21] is not that the potential energy surface is quadratic but rather that the solvation free energy of the entire ensemble of solvent molecules is a quadratic function along the "reaction coordinate". This assumption, which is the statistical mechanical counterpart of the dielectric polarization being proportional to an external field, is much milder than assuming harmonic potential energy surfaces. Recent evidence, based on molecular calculations, has appeared for an approximate quadratic free energy behavior for such systems, in the work of Warshel[22] and of Calef and Wolynes.[23]

The topics considered in this paper concern three aspects of electron transfer. Other aspects, such as orientation effects on electron transfer,[24] reactions at various interfaces and micelles, relation of some of the concepts

to those in proton transfers, and relation to gas phase electron transfer rates,[25] are among the interesting ones being explored currently.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the support of this research by the Office of Naval Research and the National Science Foundations. The present article is No. 7569 from the Department of Chemistry.

REFERENCES

1. R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta* **811**, 265 (1985).
2. R. A. Marcus, *Chem. Phys. Lett.* **133**, 471 (1986).
3. (a) H. Sumi and R. A. Marcus, *J. Chem. Phys.* **84**, 4894 (1986); (b) R. A. Marcus and H. Sumi, *J. Electronanal. Chem.* **204**, 59 (1986): (c) H. Sumi and R. A. Marcus, *J. Chem. Phys.* **84**, 4272 (1986).
4. W. Nadler and R. A. Marcus, *J. Chem. Phys.* **86**, 0000 (1987) (April issue).
5 I am indebted to Dr. W. W. Parson who calculated these various edge-to-edge distances, using the coordinates provided by J. Deisenhofer and H. Michel.[7]
6. (a) Extensive citations to the literature are given in Refs. 1 and 2 above. (b) Further work includes that of W. W. Parson, S. Creighton and A. Warshel, in *Taniguchi Foundation Symposium*, ed. T. Kobayashi (Springer-Verlag, 1987), among others.
7. References to the now classic work of H. Michel, J. Deisenhofer *et al.* are given in Refs. 1 and 2 above. Further crystallographic work has appeared in H. Michel, O. Epp and J. Deisenhofer, EMBO J. **5**, 2445 (1986); J. P. Allen, G. Feher, T. O. Yeates, D. C. Rees, J. Deisenhofer, H. Michel and R. Huber, *Proc. Natl. Acad. Sci. U.S.A.* **83**, 8589 (1986); C.-H. Chang, D. Tiede, J. Tang, U. Smith, J. Norris and M. Schiffer, *J. Mol. Biol.* **186**, 201 (1985), and *FEBS Lett.* **205**, 82 (1986).
8. Extensive citations to this literature are given in Ref. 1.
9. S. L. Mayo, W. R. Ellis, Jr., R. J. Cruchley and H. B. Gray, *Science* **233**, 948 (1986); H. B. Gray, private communication.
10. N. S. Hush, M. N. Paddon-Row, E. Cotsaris, H. Oevering, J. W. Verhoeven and M. Heppener, *Chem. Phys. Lett.* **117**, 8 (1985).
11. J. W. Verhoven, M. N. Paddon-Row, N. S. Hush, H. Oevering and M. Heppener, *Pure & Appl. Chem.* **58**, 1285 (1960).
12. S. S. Isied, A. Vassilian, R. H. Magnuson and H. A. Schwarz, *J. Am Chem. Soc.* **107**, 7432 (1985).
13. V. Kronganz, R. D. Huddleston and J. R. Miller, to be published.
14. References to this literature, both experimental and theoretical, are given in Refs. 3 and 4.
15. This result can be inferred, as an approximation for the plot of log $\tau_b k_e$ vs log $k_e \tau_L$ for $\Delta G^*/k_B T = 0$ and $\lambda_i / \lambda_o = 0$ in Fig. 2 of Ref. 3b and Figs. 1 and 4 of Ref. 4.
16. I. Rips and J. Jortner, *Chem. Phys. Lett.* **133**, 411 (1987).

17. E. g., N. W. T. Woodbury and W. W. Parson, *Biochim. Biophys. Acta* **767**, 345 (1984).
18. Refs. 47, 49 and 50 (Dogonadze *et al.*, Kestner *et al.* and Ulstrup and Jortner) in Ref. 1.
19. Refs. 52,55, and 56 (Efrima and Bixon, Siders and Marcus, Warshel) in Ref. 1.
20. R. A. Marcus, *J. Chem. Phys.* **81**, 4494 (1984).
21. R. A. Marcus, *J. Chem. Phys.* **43**, 679 (1965).
22. A. K. Churg, R. M. Weiss, A. Warshel and T. Takano, *J. Phys. Chem.* **87**, 1683 (1983).
23. D. F. Calef and P. G. Wolynes, *J. Chem. Phys.* **78**, 470 (1983).
24. R. J. Cave, P. Siders and R. A. Marcus, *J. Phys. Chem.* **90**, 1436 (1986).
25. D. E. Richardson, *J. Phys. Chem.* **90**, 3697 (1986).