THE SECOND R. A. ROBINSON MEMORIAL LECTURE

Electron, Proton and Related Transfers*

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Past and current developments in electron and proton transfer and in related fields are described. Broad classes of reactions have been considered from a unified viewpoint which offers a variety of experimental predictions. This introductory lecture considers various aspects of this many-faceted field. A simple equation is given for a highly exothermic electron-transfer reaction.

1. INTRODUCTION

In the early days of electron transfer one text which I found particularly helpful was Robinson and Stokes, *Electrolyte Solutions*.[1] It provided an overview, as well as a detailed and current picture of electrolyte solutions, to one newly arrived in the field. It is a real pleasure to acknowledge in this Memorial Lecture my debt to Professor Robinson.

In the intervening years a number of Faraday Society Discussions related to the subject matter of the present Discussion have been held, including those on Oxidation–Reduction Reactions (1960), Proton Transfer Processes (1965) and Electrode Reactions (1968). The present Discussion embraces all three and so emphasizes a trend whereby a formalism has been developed which attempts to unify the three different fields and which has now been extended to an increasingly broad class of reactions in chemistry. We survey some of the developments in this area in the present lecture.

2. WEAK-OVERLAP ELECTRON TRANSFERS

One of the virtues of studying simple weak-overlap electron transfers has been the absence of bond-breaking and bond-forming processes, with all their attendant uncertainties regarding the potential-energy surface in the transition-state region. In this way it was possible, with approximate models for the coordination shell and for the solvent outside it, to allow for the reorganization prior to and following the electron-transfer act.[2,3] Libby, in his pioneering and stimulating suggestion on the application of the Franck–Condon principle to electron transfer,[4] thought of the coordination shell and other changes as arising from a vertical transition, as in spectroscopy, rather than of a prior reorganization.[3] We introduced, instead, a prior and post reorganization. The ensuing history of the field has been nicely summarized in several recent articles, for example ref. (5)-(11).

The apparent simplicity of the weak-overlap electron transfer reaction, and certainly of the model, permitted a detailed analysis,[12-17] of topics such as the effect of driving force (ΔG°) on the reaction rate, effect of molecular parameters and of

solvents (when not specifically interacting with the reactants) on the rate,* relation between cross-reaction rates and those of isotopic exchange reactions, relation of homogeneous reaction rates to charge-transfer spectra,[18] chemiluminescent electron transfers,[19] relation to electrochemical electron transfers,† effect of driving force (activation overpotential) on the electrochemical rate constant and effect of amount of charge transferred.   The interaction between experiment and theory in these fields has provided an exciting experience, a source of pleasure and occasionally of dismay. In the late 1950s and early 1960s I visited Brookhaven National Laboratory and spoke often with Dick Dodson and Norman Sutin, who were doing pioneering experiments in the field.   Those visits were particularly stimulating.   Taube was of course making giant strides, but at that time I did not have much contact with him.

Chemistry, of course, embraces much more than electron-transfer reactions, and it became natural to think about the relation of the formalism developed for weak-overlap electron transfers to other more complicated reactions.[20-23]   The main ingredients of the formalism include work terms, w^r and $-w^p$, not necessarily coulombic, for bringing the reactants together and for separating the products, the intrinsic barrier $\lambda/4$ (additively related for the cross-reaction to those of isotopic exchange reactions), and the standard free energy of reaction of the elementary electron-transfer step, ΔG°,[12-17]

$$k \approx \kappa Z \exp\left(-\Delta G^\ddagger/kT\right) \tag{1}$$

where, in a classical treatment of the nuclear motion,

$$\Delta G^\ddagger = w^r + \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ\prime}}{\lambda}\right)^2 \tag{2}$$

with $\Delta G^{\circ\prime} = \Delta G^\circ + w^p - w^r$. κ describes the non-adiabaticity of the reaction ($\kappa \approx 1$ for an adiabatic reaction) and Z is the bimolecular collision frequency.   Analogous equations are obtained for unimolecular reactions, for electrochemical reactions, and for reactions at an interface, in which each reactant is in a different phase. Z is replaced by the appropriate analogue in each case, and in the electrochemical case ΔG° is replaced by the activation overpotential.

3. OTHER CLASSES OF REACTIONS

Any extension of the concepts of electron transfer to other classes of reactions must be aware of the differences.   In atom-transfer reactions, for example, simultaneous bond breaking and forming occur and cannot be treated by a pair of intersecting harmonic-oscillator potential-energy or quadratic free-energy surfaces.   For this reason a rather different simple model was considered,[23] one which originated with Harold Johnston (BEBO).[24]   When further simplified (with potential energies replaced in an intuitive way by free energies—forward and reverse rate constants obey microscopic reversibility)[23] and with work terms added, this yielded eqn (1), with $\Delta G^\ddagger$ now given by

$$\Delta G^\ddagger = w^r + \frac{\lambda}{4} + \frac{\Delta G^{\circ\prime}}{2} + \frac{1}{2}\frac{\Delta G^{\circ\prime}}{y}\ln\cosh y, \quad y = 2\Delta G^{\circ\prime}(\ln 2)/\lambda \tag{3}$$

and with λ having the additivity property as before.

Provided that $|\Delta G^{\circ\prime}|/\lambda$ is less than and not too close to unity, this expression is well represented by the slightly simpler quadratic expression, eqn (2).[23]   Eqn (3) or,

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* A useful recent summary is given by M-S. Chan and A. C. Wahl in *J. Phys. Chem.*, 1982, **86**, 126.
† An up-to-date account is given by M. J. Weaver in *J. Phys. Chem.*, 1980, **84**, 568.

more usually eqn (2), has now been applied to atom transfers, proton transfers, methyl-radical transfers, hydride-ion transfers[25] and concerted proton transfers.[26] An excellent review of the field has been given by Albery.[27]

In the electrochemical proton-transfer case two alternative opinions, discussed here by Krishtalik,[28] have arisen, and an effort at a unifying theory which included both as limiting cases was made.[29] Several central questions are those such as the following: how far does the proton jump, and hence how much solvent rearrangement has to occur? (In electron transfers, the centre-to-centre jump distance is always quite large, even when the reactants are in van der Waals' contact.) When is the reaction coordinate in the transition-state region the protonic coordinate and when, as expected for sufficiently highly exothermic and thereby barrierless reactions, is it the intermolecular separation coordinate for the two reactants?

4. QUANTUM EFFECTS

Quantum corrections to eqn (1) and (2) are relatively minor at room temperature for typical reactions in the ' normal region ' ($|\Delta G^{\circ\prime}| < \lambda$), for example see ref. (30) and (31). The corrections become larger in the inverted region and at low temperatures. The classical eqn (1) and (2) have a simplicity which facilitates their application to and testing by experiment. In some cases, for example in the cross-relation between the rate constants of cross-reactions and those of isotopic exchanges, it has been possible as a result to eliminate by cancellation the individual molecular properties, and so relate the rate constants to each other and to the equilibrium constant (the ' cross-relation ').[12-14]

To illustrate some of the features of the quantum-mechanical rate expression we consider for simplicity the case of a very highly exothermic non-adiabatic reaction. In the quantum theory of non-adiabatic electron transfer reactions Levich and Dogonadze[32] adapted to the problem, as they pointed out, an earlier result of Kubo and Toyozawa[33] developed for other processes. The theory and its ensuing development employs what is now known as the theory of radiationless transitions.[5-11] The rate constant for electron transfer between fixed sites is given by

$$k = \frac{2\pi |V^2|}{\hbar} \text{ (F.C.)} \tag{4}$$

where we use the notation of Bixon and Jortner in this discussion. (F.C.) is the Franck Condon factor and V the matrix element for the electron transfer transition. One problem in electron transfers in polar media, as compared with radiationless transitions involving only intramolecular vibrations, is that the former can have huge entropies of reaction. The latter are not adequately modelled by quadratic potential-energy functions, even though a suitable and applicable free-energy function may be fairly quadratic as a function of some charging parameter. As a result, an approach has been adopted in which the classical expression eqn (2), which does allow for large possible entropy changes, is introduced into the solvent contribution in (F.C.), to replace a quadratic potential-energy expression there.[34]

For the case in which the intramolecular vibration frequencies are high enough, and the reaction sufficiently exothermic, (F.C.) is given by

$$\text{(F.C.)} = \sum_{v=0}^{\infty} \mathrm{e}^{-S} \frac{S^v}{v!} \frac{\exp[-(\Delta G^{\circ} + \lambda_0 + v\hbar\omega)^2/4\lambda_0 kT]}{(4\pi\lambda_0 kT)^{1/2}} \tag{5}$$

where, for notational brevity, the oscillators have been taken to have a common

angular frequency ω. S is the contribution λ_i of these vibrations to the λ of section 2, in units of $\hbar\omega$, and λ_0 is the contribution to λ of the solution outside the coordination shell. One sees that the effect of the high-frequency vibrations in this highly exothermic case is, like λ_0, to absorb large amounts $v\hbar\omega$ of the excess energy. In effect, it reduces this exothermicity and makes the reaction faster than would be the case if none were absorbed ($v = 0$).

Eqn (5) is, of course, still a little cumbersome, although if each of the molecular parameters is known or guessed at it is rapidly and painlessly computed. There are approximations which we can introduce, which reduce the sum in eqn (5) to a single term: We replace $v!$ by a continuous function, the gamma function, $\Gamma(v + 1)$, replace the sum by an integral over v, and treat the integrand as a Gaussian about some maximum, which for convenience we will denote by v itself. If $\Gamma(v + 1)$ is then replaced by Stirling's formula, one obtains *

$$\text{(F.C.)} \cong e^{-S} \frac{S^v \exp[-(\Delta G^\circ + \lambda_0 + v\hbar\omega)^2/4\lambda_0 kT]}{\Gamma(v + 1)\hbar\omega} \tag{6}$$

where v is the solution of a transcendental equation, which when approximated by one iteration simplifies to

$$v = \frac{-\Delta G^\circ - \lambda_0}{\hbar\omega} - \frac{2\lambda_0 kT}{(\hbar\omega)^2} \ln \frac{(-\Delta G^\circ - \lambda_0)}{S\hbar\omega}. \tag{7}$$

A comparison of eqn (5) and (6) is given in table 1, where the approximate eqn (6) is seen to yield reasonable agreement over the range of parameters studied. When the

TABLE 1.—COMPARISON OF ' EXACT ' AND APPROXIMATE FRANCK–CONDON FACTORS

$-\Delta G^\circ_\lambda$ [a] /cm^{-1}	λ_0 /cm^{-1}	S	exact [b] /10^{12} cm^{-1}	approx. [b] /10^{12} cm^{-1}	approx. [c] /10^{12} cm^{-1}
14 500	500	0.655	1.0	0.9	0.8
	1000	0.600	1.6	1.8	1.7
	1500	0.545	3.3	3.7	3.3
	2000	0.490	6.4	8.0	6.4
	2500	0.435	12.4	18.3	12.4

[a] $\Delta G^\circ_\lambda \equiv \Delta G^\circ + \lambda_0$; $\hbar\omega = 1350$ cm^{-1}, $T = 298$ K; [b] exact $\equiv$ eqn (5) and approx. $\equiv$ eqn (6), and (7); [c] see text.

transcendental equation for v is solved exactly and when Stirling's formula is avoided, the last column of table 1 is obtained.

The linear dependence of $\ln k$ on ΔG° for these highly exothermic reactions, the well known energy-gap law,[35] is also seen from eqn (6) and (7) (cf. steepest descent type of derivation of that law): replacement of $\Delta G^\circ + v\hbar\omega + \lambda_0$ in the exponent in eqn (6) by the logarithmic term in eqn (7) largely removes that ΔG°, while linear dependence on v of the exponent of $S^v/\Gamma(v + 1)$, i.e. in $(S/v)^v$, and roughly of v on ΔG° via eqn (7) yields the gap law. An equation similar to but, as the authors note, different from our eqn (6) has been obtained in ref. (36).

Eqn (6) and (7) are applicable, incidentally, to recent results relating the rate of radiationless transitions to the energy gap and to solvent effects.[36] Apart from an

* More precisely, the $\hbar\omega$ in the denominator in eqn (6) has a cofactor $\{1 + 2\lambda_0 kT/v(\hbar\omega)^2\}^{\frac{1}{2}}$, which is close to unity for the systems in table 1. (v was typically between 6 and 10.)

entropic term $-(\Delta G^\circ + \lambda_0)$ is the energy of the $0{\to}0$ transition, and so the equations relate the rate constant to the frequency of that transition.

We turn next to other experimental results in the inverted region.

5. THE INVERTED REGION

Outside the range $|\Delta G^{\circ\prime}| < \lambda$ there is a considerable difference between eqn (2) and (3). Whereas eqn (2) shows a decrease of rate with increasing driving force in the inverted region (*i.e.* in the region where $|\Delta G^{\circ\prime}|/\lambda > 1$), eqn (3) displays no such phenomenon. This difference is readily understood when one considers how the potential surface leading to eqn (2) differs from that leading to eqn (3).

While the quantum corrections to eqn (1) in the inverted region significantly reduce the inverted effect, unless the relevant vibration frequencies are sufficiently low, they do not eliminate it. The inverted effect was predicted [3] in 1960. Its analogue in radiationless transitions, the energy-gap law of Siebrand,[35] is well known. The search for examples of the inverted effect in electron-transfer reactions during the ensuing twenty-odd years has, perhaps because of its novelty, been a very active one. Examples where the effect has been reported have sometimes involved a two-phase reaction, *e.g.* where one reactant is in a micelle [6,37,38] or is a semiconductor electrode [39] and the other is outside, or a reaction in frozen medium.[40] (To see the second of these [40] amid a lot of scatter it is necessary to divide the reactants into subgroups.)[41] The effect has also been invoked to explain the apparent slowness of the back reaction in bacterial photosynthesis.[42] In this reaction the bacterial chlorophyll dimer cation and bacterial pheophytin anion are fixed, presumably, rather than mobile, in the membrane. The inverted effect has also been invoked to explain the relatively larger rate constant estimated for forming a triplet state in this back reaction, compared with that estimated for the back reaction forming the ground-state singlet.[42]

In the case of bimolecular reactions in solution Bard has ascribed to the inverted effect the nearly 100% yield of electronically excited products he observed in some reactions, rather than of ground-state products.[43] Creutz and Sutin earlier reported vestiges of the inverted region.[44] In the reaction of electrons with solutes in hydrocarbons, ΔG° was varied by changing the solvent, and the results provide some evidence for an inverted effect.[45-47]

Apart from these examples the search for the effect in bimolecular reactions in solution has yielded, instead, a constant diffusion-controlled value at very negative ΔG°, as exemplified in ref. (48)-(54). Effects which can thwart the observation of an inverted region in bimolecular solution reactions are several-fold: masking by diffusion control, the existence of alternative mechanisms, such as reaction *via* exciplexes,[55] atom transfer, or formation of electronically excited products, which reduces the magnitude of ΔG° for the elementary step. Picosecond studies have been proposed to reduce the diffusion-control effect.[56] The atom-transfer alternative can be reduced in attractiveness by keeping the reactants physically separated in different phases or in a frozen medium, by holding them apart by rigid chemical bonds or by using a suitable choice of reactants with atoms which cannot undergo atom transfer.

There is a predicted relationship between the inverted region and the high-frequency tail of the related charge-transfer spectrum, when the weak-overlap and Condon approximations can be made for both.[56] When that high-frequency tail is not obscured by a new absorption band it should be quite revealing of what to expect for the related thermal electron-transfer rate constant in the inverted region in this weak-overlap case.

6. EFFECT OF SEPARATION DISTANCE

One of the newer areas of interest has been the effect of separation distance r on the rate of electron transfer. This effect, which provides a connection between geometry and rates, has been of considerable interest in biological electron transfers, *e.g.* ref. (57). Here, reactants, more or less fixed in a membrane may not have the close contact that they do in solution, and their electron transfer rate may be dominated by this factor. Efforts are being made, by building rigid bridges, for example, to study the effect of r on the rate. Another approach involves the study of reactions in frozen media: The nearest reactants react first, and the kinetics have a peculiar dependence on time: when the rate constant at an edge-to-edge separation distance r, $k(r)$, behaves as

$$k(r) = k_0 e^{-\alpha r} \qquad (4)$$

the unreacted fraction of one reactant varies with time roughly as $(\ln k_0' t)^3/\alpha^3$. [A simple derivation is given in ref. (58).] $k_0' = k_0 \exp(\alpha R_0)$, where R_0 is the distance of closest approach. In a reaction between an aromatic molecule and an aromatic anion α has been estimated [59] to be of the order of 1.1 Å^{-1}.

The application of this result to a biological electron transfer between cytochrome c and cytochrome c peroxidase provides an interesting example of a current and early connection between the two fields. From a knowledge of the structure of each component and estimates based on bringing the opposite charges near each other and aligning the hydrogen bonds, the haem–haem edge-to-edge distance r has been estimated to be *ca.* 16.5 Å.[60] (The latter may be compared with the value of 14.3 Å based on a quite different type of estimate, fluorescence quenching.)[61] The minimum rate of electron transfer between the two haems (minimum because this step may not be the rate-limiting one) is *ca.* 10^4 s^{-1}. (T. Yonetani and J. Yandell, personal communication.) The maximum rate of electron transfer is, at close contact, *ca.* 10^{13} s^{-1}. Multiplying this by $\exp(-\alpha r)$ yields a maximum calculated rate constant of $10^{13} \times 10^{-8}$ or 10^5 s^{-1}, which is to be compared with the experimental lower bound of 10^4 s^{-1}.* Thus these two rate constants are consistent. However, a not much higher α, or a not much larger r, would not fit in. The point of this exercise is not to compare the current extent of quantitative agreement but to indicate that when better estimates of α, of haem–haem edge-to-edge separation distance, of orientation effects, and of rate constants become available, there will be interesting and useful comparisons to be drawn.

A word about the assumed 10^{13} s^{-1} for the maximum value of the k_0 is perhaps in order: J. R. Miller (personal communication) estimated from his experimental data that the maximum k_0 for reactions between molecules and/or ions was *ca.* 10^{14} s^{-1}, or somewhere between 10^{13} and 10^{14} s^{-1}. (He used data obtained near the maximum of the $\ln k$ against $\Delta G°$ plot. He extrapolated yield against time data some six orders of magnitude from data obtained over nine orders of magnitude.) I have chosen a value of 10^{13} s^{-1} so that eqn (4) will yield at $r = 0$ the maximum it can be, which is the frequency of nuclear motion, 10^{13} s^{-1}. If, experimentally, k_0 proves to be 10^{14} s^{-1}, eqn (4) can still be used but will break down for r values below that given by $\exp(-\alpha r) = 10^{13}/10^{14} = 0.1$, the reaction then becoming adiabatic at that r (*ca.* 2 Å).

7. THIS DISCUSSION

The papers in this Discussion describe many facets of this field of electron and proton transfer. Many of the points touched upon in the previous sections, and more,

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* Also included is a nuclear tunnelling factor which typically varies from 1 to *ca.* 5 at room temperature. The classical factor is of order 10^{13} s^{-1}.

are well illustrated by the papers of this symposium. Kuznetsov, Kuznetsov and Ulstrup, Bixon and Jortner, and Friedman and Newton consider various quantum-mechanical and other theoretical aspects of the problem. The calculations focus on the polarized solvent, the vibrations and the electronic structure, with different emphases.

The comparison of the theory described earlier with experiments on electron exchange reactions is discussed by Brunschwig *et al.* Experimental work on homogeneous electron transfers is presented by Bruhn *et al.* on the effect of added salts, by Amouyal *et al.* on electron transfer from various photoexcited organic molecules, and by Huppert *et al.* on intramolecular electron transfer.

Electron transfer at interfaces is discussed by Savéant and Tessier, who describe the relation between the observed dependence of the electrochemical transfer coefficient on overpotential and the theory of section 2, and by Willig and Charlé, who treat electron transfers between ions and molecules adsorbed on organic electrodes.

Proton transfers are treated at electrodes by Krishtalik (the hydrogen evolution reaction), who discusses some of the controversy referred to earlier. In solution they are treated by Limbach *et al.* (isotope effects and double proton transfers) and by Albery, who analyses the concerted proton-transfer problem. Hydride transfers are also discussed in relation to the theory of section 2 by Roberts *et al.*, while Caldin *et al.* examine the effect of polar solvents on hydrogen-atom transfers.

The complexity of proteins and of biological molecules generally requires an increasingly detailed knowledge of the structure, to make the interpretation of the electron-transfer rates as meaningful as possible. Structural and other aspects are described for cytochrome c by Roberts *et al.* The electron transfer reaction of cytochrome c on a modified metal electrode (adsorbed organic layer), and its relation to physiological redox reactions is discussed by Eddowes and Hill. Homogeneous electron transfers of cytochrome c, with emphasis on entropy and volume of activation, are treated by Heremans *et al.*

Proton transfers in biological systems are equally important, and are discussed in the paper of Rich (together with electron transfers), Gavach *et al.*, and Kell and Hitchens. The coupling between electron transfers, proton transfers and ATP synthesis represents, of course, a particularly important problem, and one which has been the subject of different views. These are touched upon in this part of the Discussion. The general area reflects the trend towards an increasing knowledge of structure, kinetics and thermodynamics, and increasingly fast and accurate experimental methods. Perhaps guided by results obtained in the simpler systems described in earlier parts of this Discussion, we can look forward to striking developments.

The Organizing Committee is to be congratulated for having arranged such a broad and interesting programme. The posters, contributions which I have not had a chance to see beforehand but whose content is hinted at by the titles, add their strength to this broad Discussion of Electron and Proton Transfers. The Organizing Committee has done its part. It remains for us to begin.

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