Light-Induced Charge Separation in Biology and Chemistry, eds. H. Gerischer and J.J. Katz, pp. 129-149. Berlin: Dahlem Konferenzen 1979.

Mechanisms of Charge Separation and Subsequent Processes
Group Report

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THEORETICAL CONSIDERATIONS

The theoretical aspects of charge separation were discussed in this group and reexamined, in particular with respect to tunneling (cf. Grätzel et al., this volume).

Basically three theories approach the general problem of rate reactions and are potentially applicable, among other processes, to electron, proton, or H-atom transfer, as long as these are "one step" processes. The best known treatment and the most widely referred to in the literature (because it is best understood by the experimentalist) is the one elaborated by Marcus (15). This theory is considered classical because the nuclear motions are treated on a classical basis, quantum mechanics being applied to the èlectron motion.

A quantum theory of charge separation was developed by Levich and Dogonadze (13) and extended by later researchers to treat more than one vibrational frequency. Recently this problem was approached on essentially the same basis by Jortner (12). A related route, referred to below as semiclassical, was described by Hopfield (11), who in effect evaluated the Franck-Condon vibrational factors in an approximate way (see Marcus, this volume).

In the case we are now considering, experimental data furnish evidence for two types of relations concerning the rate constant, k, of a reaction as a function of kinetic and thermodynamic properties. The most widely used of these is the Arrhenius plot.

The theoretical predictions yield the relations schematically represented in Figs. 1 and 2.

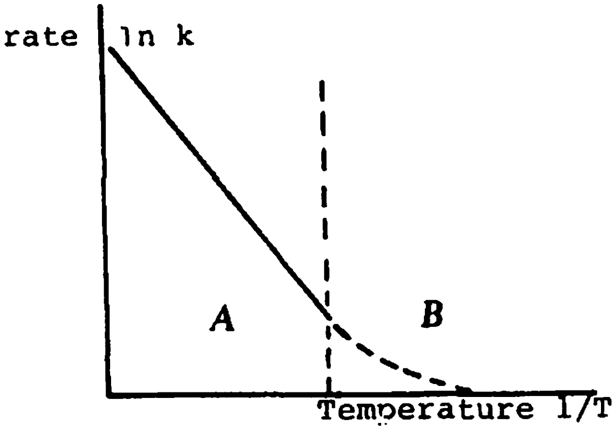

FIG. 1 - Typical variation of the rate constant k of a reaction as a function of temperature. The vertical dashed line separates the high temperature limit in which the rate is classically controlled (A) from the low temperature limit (B) where the rate is quantum controlled.

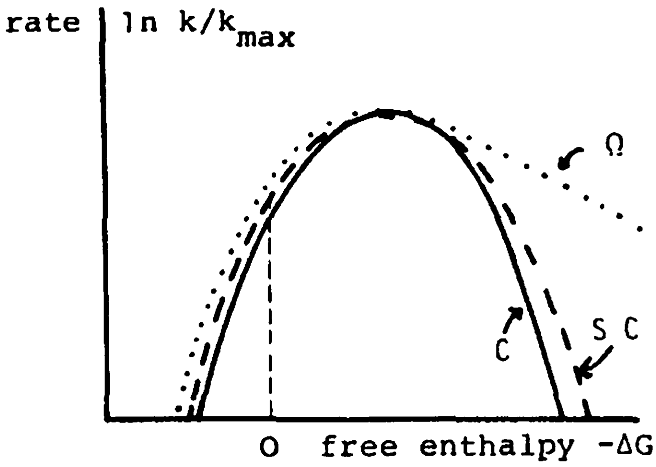

FIG. 2 - Calculated reduced rate k/k_{max} as a function of the one step reaction. The ratio k/k_{max} is used to normalize the curves for the three treatments: C, classical; SC, semiclassical; and Q, quantum.

In Fig. 2 the classical plot (C) is a parabola, as is the semiclassical (SC) with a somewhat smaller curvature, while the quantum curve (Q) is asymmetric. Depending on the reduced values of the various frequencies of motion, $h\nu_i/2kT$, the curves for the three treatments are similar to or different from each other.

How do the experimental data, when available for single step reactions, fit these predictions? We have not dwelt on the Arrhenius plots that were obtained from experiments in flash photolysis, pulse radiolysis, stopped flow... etc., as a function of temperature. We would, however, like to add a word of caution for cases where rates independent of temperature are found. These may or may not point to a tunneling effect, depending on whether the reaction proceeds in a single step or whether multiple reactions are involved, in which compensating effects can appear.

Few reliable studies have been made of strongly exoenergetic reactions that relate the rate to the free enthalpy (also called free energy or simply the Gibbs function), ΔG, of the overall reaction.

Fluorescence quenching experiments have been interpreted by Rehm and Weller (21,22) as electron transfer between aromatic compounds in which one compound acts as donor, the other as acceptor. The results are plotted in Fig. 3. The data fit the parabolic form of the equation if ΔG is not too negative, but obviously fail at very negative values of ΔG where a diffusion-controlled limiting rate appears. The expected fall-off in rate is not observed.

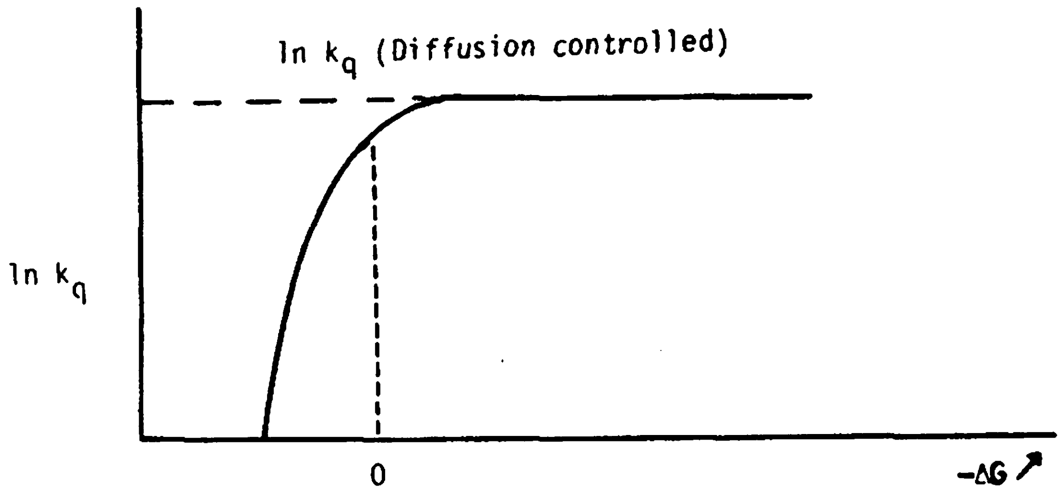

FIG. 3 - Plot of ln k_q as a function of increasing negative value of ΔG.

A possible explanation is that the electron transfer that quenches the fluorescent state does not occur in a single step. It is known that exciplex formation may mediate the electron transfer, and Weller (26) suggested that in processes where ΔG is large exciplex formation may provide an intermediate step that has to be taken into account in formulating the mechanism.

New systems should be looked for in which exciplex formation is inhibited, as in molecules bearing the electron acceptor at one end and the donor at the other end of a rigid structure, such as those studied by Davidson et al. (6), or where exciplex formation is unlikely, as in some coordination compounds.

An interesting point was raised about the pre-exponential factor in relation to collision rates of reacting molecules and/or the fluctuations of the surrounding dipoles of the solution cage, which influence the positions of the electronic energy levels of charged species that react in fluid media.

Weller (in preparation) reports intramolecular electron transfer fluorescence quenching experiments in solvents of widely different dielectric relaxation times (about 4 ps for acetonitrile, $\geq$100 ps for propanol) which yield rates of electron transfer that are approximately in the inverse ratio of the dielectric relaxation times in these two solvents. Further experiments should be done along these lines.

We did not really address the question whether or not slow or fast electron tunneling rates can be inferred from the experimental data. Two sources of information are the Arrhenius pre-exponential factor (when there are no other contributions to the usual $10^{13}\ s^{-1}$ or $10^{11}\ \ell mole^{-1}\ s^{-1}$ factors for unimolecular and bimolecular reactions) and charge transfer spectra (see Marcus, this volume). An example is the reaction:

$$\text{Cyt c}^{II} + \text{BChl}_2^{+} \longrightarrow \text{Cyt c}^{III} + \text{BChl}_2$$

for which the pre-exponential factor is of the order of

10^9 to 10^{10} s^{-1}, indicating slow electron tunneling unless there are other contributing factors.

EFFICIENCY OF LIGHT-INDUCED CHARGE SEPARATION

A long discussion arose about the way one can arrive at the fraction or an upper limit on the fraction of absorbed photon energy stored and the corresponding ratio for power delivered in an external circuit when charge is continuously separated. Such a calculation involves two clearly separate issues of thermodynamic efficiency and more specific efficiencies (η_θ and the remaining four factors given in Knox's paper, this volume).

It was recalled that on the thermodynamic side, matters of principle were largely settled in 1959-1967 (Knox, this volume). However, since the foundations of the subject remain conceptually difficult, they are frequently regenerated in the literature and were vigorously debated here (3). At light intensities of interest to solar energy conversion, the 30% loss of free energy can be traced to loss of directionality,* whether by scattering or by the absorption act itself. This was emphasized in the discussions.

With respect to specific factors, the spectral efficiency, η_S, appears to be the one of the most interest to our subject because the design of a charge separator can be controlled by choosing appropriate energy level distributions and spectra.

It was felt that continued efforts should be made to apply the potentially decisive thermodynamic limitations to real systems. These are relevant when there is a known quantum requirement for an energy-producing photoprocess in the steady state. In

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*Blackbody radiation is not directional, whereas solar radiation has direction as it penetrates the earth's atmosphere. Hence, it is not blackbody and no temperature can be associated with it. To define a temperature and to be able to apply the Carnot Cycle, the solar light, which is at much lower temperature than the initial blackbody source (the sun), has to be randomized.

green plants the quantum requirement of at least 8 per O_2 molecule (2) is not in conflict with a predicted η_θ = 69%. In bacteria the limitation is more severe, η_θ = 57%, but there is no corresponding overall quantum requirement available for comparison. These numbers can be accounted for using Equation 11 in Knox's paper (this volume) and data quoted in reference 5 of his paper:

$$\eta_\theta \text{ (chloroplast system)} = 1 - \frac{295}{1148} - \frac{0.025}{1.83} \ln \frac{1}{0.03} = 0.69$$

$$\eta_\theta \text{ (Chromatium)} = 1 - \frac{295}{839} - \frac{0.025}{1.39} \ln \frac{1}{0.01} = 0.57$$

The radiation intensity assumed in the two cases is reflected in the radiation temperatures (1148 and 839 K, respectively) which vary considerably with wavelength (see Table I of Knox's paper, this volume). Note that the thermodynamic "limitation" varies, though slowly, with respect to intensity as the following expression, equivalent to Eq. 11 of Knox's paper (this volume), shows:

$$\Delta G = E_1 + k_B T \,\ell n \left[\frac{IB + L \exp(-E_1/k_B T)}{A + L + IB}\right], \text{ (At all light intensities)}$$

where E_1 is the excited state or band gap energy, I (in $m^{-2}s^{-1}$) is the photon flux, B (in m^2) is the absorption cross section, and A and L (in s^{-1}) are the radiative and nonradiative de-excitation rate constants. This expression has limiting values of zero when I is taken as that of the blackbody background at temperature T, and has the value E_1 when I goes to infinity, i.e., when the levels saturate. Between these limits lies the range of usual interest in which the exponential term proportional to L and the term IB in the denominator may be dropped, leaving the more familiar equation

$$\Delta G = E_1 + k_B T \,\ell n \left(\frac{IB}{A+L}\right) . \text{ (At moderate light intensity)}$$

Among the more specific efficiency factors, η_S is appropriate to describe the improvements obtained by combining two or three theshold converters in series with graduated absorption thesholds. Although each system will have its own design limitations, it may be worthwhile to consider the relation existing between these systems and the one developed by green plants (Systems I and II). As more rate constants and operating potentials become known in the electron transfer chains, it will be useful to keep track of how much of η_L is to be retained as a rough parameter and how much can be combined into the more explicit format of η_0 (cf. (23)).

DEFINITION AND DETERMINATION OF REDOX POTENTIALS OF EXCITED MOLECULES

Knowledge of redox potentials of molecules in an excited state is obviously of crucial importance in light-induced processes and this question gave rise to a detailed presentation by Weller. The argument will be illustrated for the oxidation potential of an excited electron donor molecule D, which captures an electron according to the reaction:

$$D^{+\cdot} + e^- \rightleftharpoons D \qquad (1)$$

The ground state oxidation potential for this reaction is given by the expression: constant $-E_D^{ox}$, where the constant refers to the reference electrode. The excitation of the donor involves the energy change:

$$D \overset{h\nu}{\rightleftharpoons} D^* \qquad \Delta E_{o,o}\ (D) \qquad (2)$$

which corresponds to the zero-zero transition that can be obtained from spectroscopic data (for instance, from the frequency of the crossing point of the absorption and fluorescence spectra (see Fig. 4)). Addition of Eqs. 1 and 2 yields the desired half reaction:

$$D^{+\cdot} + e^- \rightleftharpoons D^*$$

for which the oxidation potential is: $\text{const-}E_{D^*}^{ox}$ (3)

with:

$$\text{const-}E^{ox} = \text{const-}E_D^{ox} + \Delta E_{o,o}(D) \qquad (4)$$

so that one can write:

$$E_{D^*}^{ox} = E_D^{ox} - \Delta E_{o,o}(D) \qquad (5)$$

Analogous considerations for the reduction potential, E_A^{red}, of acceptor molecule A lead to:

$$E_{A^*}^{red} = E_A^{red} + \Delta E_{o,o}(A) \qquad (6)$$

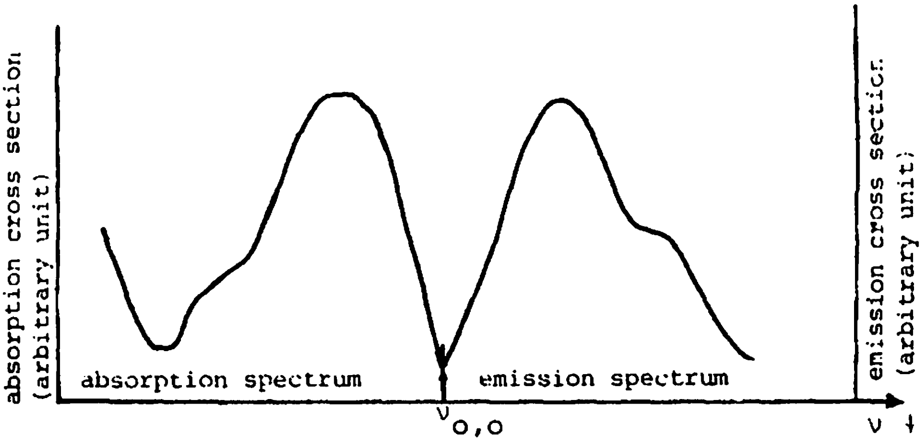

FIG. 4 - Typical absorption and emission spectra of an organic compound allowing the determination of the o,o band and thus $\Delta E_{o,o}$.

These procedures imply that only negligible entropy changes are involved in electronic excitation, so that the spectroscopically determined values of $\Delta E_{o,o}$ can be considered as free enthalpy changes, ΔG. It has been found that this requirement is fulfilled with ±0.03eV for most compounds studied (25).

The free enthalpy change, ΔG^*_{et}, connected with an excited state electron transfer (et) reaction can now be easily obtained from Eqs. 5 or 6:

$$\Delta G^*_{et} = E_D^{ox} - E_A^{red} - \Delta E_{o,o} \tag{7}$$

The question of whether electron transfer reactions are likely to be accompanied (or followed) by proton transfer can be handled in a manner quite similar to that used above for electron transfer alone. The reactions (and their free enthalpy changes) which have to be included are the proton dissociation reactions of $DH^{\dot{+}}$, the radical cation of the electron donating molecule, and of $AH\cdot$, the protonated radical of the electron acceptor:

$$DH^{\dot{+}} \rightleftharpoons D\cdot + H^+ \qquad (2.303\ RT\ pK_{DH^{\dot{+}}}) \tag{8}$$

$$AH\cdot \rightleftharpoons A^{\dot{-}} + H^+ \qquad (2.303\ RT\ pK_{AH\cdot}) \tag{9}$$

The use of appropriate thermodynamic cycles leading to the overall reactions (in the excited state):

$$DH^* + A \rightleftharpoons D\cdot + HA\cdot \tag{10}$$

or

$$DH + A^* \rightleftharpoons D\cdot + HA\cdot \tag{11}$$

gives for the free enthalpy changes ΔG^*_{ht} involved in excited state H-atom transfer reactions 10 and 11:

$$\Delta G^*_{ht} = E^{ox}_{DH} - E^{red}_{A} - \Delta E_{o,o} + 2.303\ RT\ (pK_{DH^{\cdot+}} - pK_{AH\cdot}), \tag{12}$$

where $\Delta E_{o,o}$ is the zero-zero transition free energy required for the excitation of DH or A, respectively. Typical values for aromatic phenols (DH = ArOH) and aromatic nitrogen heterocyclic compounds (A = Ar(N)) are $pK_{DH^{\cdot+}} \approx 0$ and $pK_{AH\cdot} \approx 15$, respectively so that

$$2.303\ RT\ (pK_{DH^{\cdot+}} - pK_{AH\cdot}) \approx 0.9 eV,$$

which means that additional proton transfer can considerably facilitate an electron transfer reaction between suitable electron (and proton) donor molecules and electron (and proton) acceptor molecules. As reactions 10 and 11 do not involve a net charge separation, their free enthalpy changes are virtually independent of the polarity of the medium. This makes H-atom transfer a likely redox mechanism in biological systems with low polarity environments (lipids, interior of proteins).

For application and confirmation of these considerations about excited state redox potentials and free enthalpy changes in excited state electron or H-atom transfer reactions that lead to fluorescence quenching or chemiluminescence, see references (21), (22), and (27). The well-known relations between the oxidation potential, E^{ox}_{D}, and the (adiabatic) ionization potential, IP_D:

$$E^{ox}_{D} = IP_D - \Delta G^{solv}_{D^+} - const, \tag{13}$$

and between the reduction potential, E^{red}_{A}, and the (adiabatic) electron affinity, EA_A:

$$E^{red}_{A} = EA_A + \Delta G^{solv}_{A^-} - const, \tag{14}$$

in which $\Delta G^{solv}_{D^+}$ and $\Delta G^{solv}_{A^-}$ are the solvation free enthalpies connected with the reactions:

$$D_g + D_s^+ \rightleftharpoons D_s + D_g^+ \tag{15}$$

$$A_g + A_s^- \rightleftharpoons A_s + A_g^- \tag{16}$$

(where the subscripts g and s refer to the gas phase and the solution), can be combined to yield the free enthalpy change involved in excited state electron transfer reactions according to Eq 7:

$$\Delta G_{et}^* = E_D^{ox} - E_A^{red} - \Delta E_{o,o} = IP_D - EA_A - \Delta E_{o,o} - (\Delta G_{D^+}^{solv} + \Delta G_{A^-}^{solv}) \tag{17}$$

Equation 17 shows that the difference $E^{ox} - E^{red}$ of the same molecule, rather than being closely connected (as is often said) only with the longest wavelength zero-zero transition, strongly depends on solvent polarity through the solvation free enthalpy term $(\Delta G_{D^+}^{solv} + \Delta G_{A^-}^{solv})$. For a medium-sized molecule A = D in highly polar solvents the magnitude of this term is of the order of 4eV and decreases to about 2eV as the dielectric constant approaches 2. Thus Eq. 17 also indicates that electron transfer reaction between A^* and D to yield ionic products A^- and D^+ are expected to be strongly solvent dependent and to decrease in rate with decreasing solvent polarity. Studies to confirm this prediction by the use of a wide variety of solvents are clearly required.

In the case of molecules adsorbed on a solid-state surface but not experiencing charge transfer absorption, the free enthalpy change connected with the excited state electron transfer can also be discussed on the basis of Eq. 17. It should, however, now be modified so as to contain only the solvation free enthalpy connected with the adsorbed molecule, since the solvation of the counter charge residing in the solid state material does not depend on the surrounding medium and can be neglected. The solvent effect expected for such heterogeneous systems should, therefore, be smaller than in homogeneous systems.

LOCAL FIELDS AND THEIR INFLUENCE ON CHARGE SEPARATION

From fundamental principles an electric field must be instrumental in the separation of photoproduced charges. In a trivial sense a field is needed to cause the drifting of the charges necessary to give detectable currents. In a less obvious way an electric field may be important in the act leading to free charges following the absorption of light (or the capture of any energy) at a particular site in the condensed phases.

Electric fields arise from charge distributions whose origins are quite varied:
Applied fields. These usually appear as a result of net charge deposited upon electrodes across a sample. They are usually quite homogeneous and may be treated as resulting from averaged or smooth charge densities at the electrodes.

Spontaneous electrification fields at interfaces. As is well known and was clearly restated in Albrecht's paper (this volume), when a charged species equilibrates across an interface, an interfacial potential must develop if the chemical potential of the species varies across the interface. These fields are as common in electrochemistry at the interface between electrode and electrolyte as they are, for example, in solid-state physics at interfaces between two different solids. Equilibration is reached when the electrochemical potential* of each charged species present in both phases (and capable of passing through the boundary) is equal on both sides of the interface. The charge distribution at electrode interfaces in electrochemistry is usually treated on the basis of the Helmholtz-Gouy-Chapman-Stern theory.

The discussion focused on the possible role of fields from interfacial electrification on charge separation. Thermodynamics tells us that if a charged species, j, can equilibrate over some spatial domain and experiences a different chemical potential over this domain, then a space charge must develop which results in an electric field. There are many ways for the chemical potential of a charged species to vary over an interfacial domain, e.g.: (a) difference in work function

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*For an electron, the electrochemical potential is equivalent to the Fermi level in solid-state physics and to the redox potential of a redox couple in electrochemistry.

(equivalent to a difference in redox potentials), (b) differences in affinities for ions, and (c) a difference between surface and bulk energies (free enthalpies).

Once interfacial electrification is established there can be no net flow of current. It can then be said that the electrically driven current (drift) exactly balances the diffusive flow from the concentration gradients in the equilibrating charge.

When an electron-hole pair or an ion-pair is generated in such a space charge region, the two charge carriers will respond differently to the field. The charged species will move in opposite directions and follow the gradient of the electric potential (drift) rather than the concentration gradient (diffusive), except in very unusual cases. Thus the field of spontaneous electrification will cause charge separation. Such charges can be produced by photoionization or can be photoinjected from the surface of the interface.

The fact that the drift force (and not the diffusive force) usually dominates photoproduced charge separation is an interesting and important point. This follows because the diffusive flux is proportional to charge concentration times a logarithmic gradient of concentration and, therefore, the concentration gradient. The drift flux is proportional to the charge concentration times the potential gradient. Photoproduced charge does not usually significantly change the concentration gradient, but it does increase the charge concentration, so that the drift force is the controlling one.

Two extreme types of electrification were considered for two phases, I and II, forming an interface:
Charge depletion electrification. In this case the mobile equilibrating charge is withdrawn from the interior of phase I through the interface and picked up by phase II because the chemical potential of the species in phase II is lower than in phase I.

A certain region within phase I is depleted of equilibrating charge, leaving a space charge in phase I consisting of the non-equilibrating counter charge.

Charge accumulation (or injection) electrification. The equilibrating charge is injected into phase I and accumulates there where its chemical potential is lower than in phase II. The electrification charge in phase I now consists of equilibrating charge in contrast to the case of depletion electrification.

These two extreme kinds of electrification have very different properties as reported in Albrecht's paper (this volume). From a discrete charge point of view of the two types of electrification another difference may be discerned:

1) Case A (depletion) - Intrinsically photoproduced equilibrating charges are made in the presence of counter charge. They must escape the Coulomb field to separate.

2) Case B (accumulation) - Intrinsically photoproduced equilibrating charges are made in the presence of charges of the same sign. They do not escape from Coulomb fields for separation.

In the absence of a space charge, the diffuse Onsager type of electron-hole pair separation (19) has been found to be valid in the bulk of organic solids with small dielectric constants of the order $\varepsilon = 3\text{-}4$ (4, 14); at the interface between such an organic solid and an aqueous solution or metal contact (5, 27); and in the bulk of inorganic solids such as amorphous selenium (20). In these systems electron-hole pair separation is brought about by diffusive motion out of the potential well set up by the Coulombic attraction between electron and hole in the bulk phase, or between one charge carrier and its image charge at the interface.

DISCRETENESS OF CHARGE EFFECTS

For field-sensitive phenomena occurring on a submicroscopic scale of distance in the immediate vicinity of a unique charge distribution, it is likely that the use of Poisson's equation for determining an average field is invalid, and some allowance for the discreteness of charge will have to be made. Discreteness of charge effects have been extensively discussed. These effects are most important in systems of low dielectric constant and can influence the distribution of ionic species (e.g., in adsorption at interface) or charge transfer reactions at interfaces. There are, however, also cases when a continuum model gives a surprisingly good description of an interface containing discrete charges.

Many theoreticians have noted that the discrete charge effect should be important, particularly when the charge density is low and the salt concentration is high (e.g., (18), in which the effect of discrete charges on the electrical properties of a membrane is discussed). The prediction of the importance of discrete charge effects has been tested experimentally by measuring the number of adsorbed ions when monolayers or bilayers were formed from neutral or zwitterionic lipids. In all cases a smeared charged model (Stern equation) was found to describe the experimental data obtained with the amphipathic molecules 2-(p-toluidinyl)-6-naphthalene sulfonate (TNS), sodium dodecylsulfate (SDS), and dodecyltrimethylammonium bromide (DTAB) (16,17). This conclusion has now been extended to divalent cations by the use of ^{31}P NMR (16,17).

Two cases are known experimentally where the discrete charge effect is important: (a) a single charge fixed to the mouth of a channel will influence the transport properties of the channel (Läuger, this volume) and (b) when the adsorbing ions reside within the bilayer membrane they produce what the Russian School has termed "boundary potentials" in addition to diffuse double layer potentials. Discrete charge effects are observed when lipid-soluble ions such as tetraphenylborate adsorb within membranes, presumably because large "boundary potentials" can be produced at very low charge densities (1).

It should be stressed that no adequate theory exists for an ensemble of discrete mobile charges.

MAGNETIC FIELD EFFECTS

Starting from the general qualitative presentation given in Schott's paper (this volume), the group tried to evaluate the conditions in which the study of the effects of magnetic fields facilitate the understanding of problems relating to charge separation at interfaces.

To date these effects have been used mainly to study homogeneous phase (liquid or solid) phenomena. All of these various effects are not equally suitable for the study of processes occurring at interfaces or which may be involved in charge separation.

Magnetic Field Modulation of Processes Involving Triplet States

The effects that influence electron spin interactions were discussed first. Triplet state ions aside, the triplet pair (TT) process is related to charge separation only to the extent that the triplet energy is more than half the energy needed to create a charge carrier pair (electron-hole or ions).*

In addition to this energy requirement, the reaction TT → +- should not be diffusion-limited for a modulation of the charge yield by a magnetic field to be possible.

Observation of such a modulation would then show that the process is not collision-limited and would give some information on the relative values of the rates of carrier pair formation in a singlet or a triplet state. If pairs were formed in a(n) (almost) pure state (see below), a second magnetic effect would then develop, given sufficient time before recombination or irreversible separation, and the final yield would be modulated by both effects, giving even more information about the charge generation process.

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*This is not true, unfortunately, in anthracene, the most-studied organic crystal. On the other hand, there may be cases where one triplet has enough energy to create a charge carrier pair when it encounters a suitable ground-state singlet molecule. A triplet-singlet interaction is not expected to show any magnetic field effect of the kind discussed here. However, the TT process will be felt, indirectly, in the charge carrier yield at high T densities, since it provides a decay channel for a precursor.

It seems likely that the prospect for observing such effects is better if charge separation occurs by autoionization of a neutral product of a TT interaction, rather than if charge separation occurs by direct electron transfer between the triplets (tunneling). Too strong a TT interaction, especially an admixture of charge-transfer character into the triplet pair, might force the adoption of a new theoretical approach where no (or very different) magnetic field effects would be expected. An oxygen-triplet interaction may be an example. More work, theoretical and experimental, on well-defined systems is certainly needed.

The presence of an interface separating the triplets, or to which one triplet may be fixed, would have subtle effects. For instance, the interface could restrict triplet motion to one half of the space, and the consequences of collision of triplet with interface would be revealed in spin relaxation or quenching. Here again, further research is clearly needed. Might it be of interest in micelle studies, in which case at least one triplet would stay in a limited space?

The triplet-doublet (TD) process may be significant in charge separation. Most often a ground state doublet is involved. If the doublet state molecule is neutral, the same considerations as above, with few changes, apply. Organic ions, however, are often doublets. Transfer to such an ion of the triplet energy is unimportant when the unexcited doublet and excited doublet have identical drift mobilities. An extreme case of a contrary situation is a trapped versus a free charge in an organic solid. But even in a liquid, transition of an electron from a localized to an extended state of short lifetime but high mobility might be enough to allow the carrier to overcome a surface barrier. Liquid alkanes, for instance, would have such conducting states.

Near an electrified interface, two kinds of relevant TD processes can be considered. One would be related to the interface itself, i.e., the surface separating two phases and corresponding to charge carrier injection into one medium. Most often, however, the triplet would have to cross a barrier layer and interact there with a D state molecule rather than reach the surface. This could give rise to detrapping and could change the balance between free and fixed charges in the barrier. In both cases, the current and possibly the triplet lifetime would become magnetic field sensitive.

Besides proving that triplet states are involved in charge separation, it was considered that the study of modulation by magnetic fields could tell what fraction of interactions leads to triplet quenching and which of these to charge liberation, and could possibly, in an ordered system, give some clue about how it is (spatially) distorted by the presence of a doublet. But only few relatively unambiguous experiments are available and more are definitely needed.

It was recognized that one important feature in these processes is their anisotropy in the crystalline state, which gives information about the nature and transport properties of the moving species. The effects may perhaps persist to some extent in an oriented medium, but no such system has to our knowledge ever been investigated, so that the amount of information obtainable from such systems is unknown. It may well be of interest to investigate TT interactions in a liquid crystal medium.

Our discussion showed that such methods are well suited for the study of physicochemical systems. One can think of applying them to many problems. Two examples are: (a) to the study of the photovoltaic response of thin organic films in a magnetic field and (b) to the use of these effects to probe, via triplet states, the local structure of some amorphous films. Too little attention has been paid to date to application of such methods to biological problems.

Magnetic Field Effects Due to Modulation by Hyperfine Interaction

The other class of magnetic field effects that was discussed is more directly related to charge separation, since it involves spin precession in a cation (or hole)-anion (or electron) pair that is formed in some ionization process. The effect is detected as modulation by small ($\lesssim$ 100 Gauss) magnetic fields of light emission, or an electrical current, or in the yield of a product. These reveal that some reaction rates depend on the spin state of the complex in which spin motion is occurring. Such effects are closely related to magnetic polarization (nuclear or electronic) revealed in the NMR or EPR spectra of products of several chemical reactions (CIDNP and CIDEP). For this to occur, the following conditions should be met: (a) the spin state of the pair should not be random; (b) the electron-hole exchange interaction should be small enough at least in a sufficient time interval between generation and recombination of the pair; and (c) electron and hole should experience different hyperfine interactions, which set the scale of the magnetic fields involved. The first condition is obviously met in a "geminate" pair: just after carrier generation the pair is in the same total spin state as was the precursor. Non-geminate electron-hole or ion-ion pairs recombine via a bimolecular process. Such a pair would initially, at room temperature, be found in a singlet state in 25% of the cases, in a triplet state in 75% of the cases. If recombination rates are much different in singlet and triplet pairs, a magnetic field effect may also be observed with non-geminate pairs, but its amplitude would be smaller than that observable with geminate pairs. No experiment corresponding to this situation has yet been reported.

In the last two years, the magnetic field effect on radical pairs has mainly been investigated, experimentally and theoretically, in connection with homogeneous phase phenomena. There is, however, continuing interest in phenomena occurring at interfaces. In general, the effect of the magnetic field has been observed as a field modulation of optical signals or of a current. The sensitivity of detection is very great, and for this reason the effect can be helpful when studying charge carrier pair kinetics at an interface.

Obviously, the occurrence of the magnetic field effect shows that the requirements listed above are met. In addition, one can deduce from the halfwidth of the magnetic field modulation the order of magnitude of the time interval during which spin motion occurs in a geminate pair. The magnetic field effect on the rate for irreversible separation of the electron-hole pair also yields an estimate of the ratio of the rate constants for recombination in the singlet and triplet channels.

We agreed that more precise information on these rate constants can be obtained only if sufficient experimental data are available to clearly establish the kinetic model of the electron-hole (or ion) pair and the relevant hyperfine interaction. In the initial work on sensitized delayed fluorescence (SDF), the pair was considered as a bound complex with a one-step irreversible dissociation (5). Such a model may, however, be hard to reconcile with a small enough exchange interaction within the pair. The theory was then developed to include, among other things, relative motion of the components of the pair with special emphasis on liquid phase reactions (8,9,10). More recently the two features, a finite lifetime of a bound complex and the motion of the components, have been combined in connection with a detailed experimental study of sensitized hole injection in an anthracene crystal (Mueller et al., in preparation).

To obtain improved rate constants for a given system from time-resolved or from steady state experiments, information on the dimensionality of the motion (mainly 2- or 3-dimensional) and on the electric potential in the system is needed. In the steady state experiments, the lifetime is changed by an applied electric field or through reactions that remove either the electron or the hole from the pair.

A particularly challenging problem appears to be the derivation of a satisfactory model for the magnetic field effect observed in bacterial photosynthesis.

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