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Medium Effects in Photoinduced Electron Transfer Reactions**

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The transfer of an electron between two molecules is a fundamental chemical process of great significance in biochemistry as well as in general chemistry. Electron transfer reactions can be induced by the absorption of light – as in photosynthesis – so that one of the molecules reacts through an electronically excited state; a net storage of chemical energy may then take place[28]*. When electron transfer involves molecules in condensed phase, the role of the liquid or solid medium must be considered. In the first place, a polar solvent may promote electron transfer through the stabilization of ion pairs and the separation of ions; but if the polar solvent must reorganize prior to the reaction, then an activation barrier will exist against electron transfer in polar solvents. – This article gives a critical review of this field, with some novel ideas concerning the role of the medium (liquid solvent or solid matrix) in the overall energy balance of electron transfer, in the kinetics of the reaction, and in the further process of charge separation. It is suggested in particular that no dielectric screening by a polar solvent can exist when ions are formed in direct contact; and that the extensive reorganization of the solvent prior to electron transfer is so unlikely as to be discounted. In these respects the model presented in this article diverges from the commonly accepted models of Weller and of Marcus and Hush. In the Conclusion section some areas of particular importance for further research in this field are outlined.*

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1. Introduction

Electron transfer (ET) processes in general, and photoinduced ET processes in particular, are among the most fundamental of all chemical reactions and for this reason they have been the object of very active research[1]. Since most of chemistry (and all of biochemistry) takes place in condensed media – liquids and solids – the influence of the medium is of great importance for an understanding of the mechanism of ET processes. This influence comes in at several stages, and these we shall consider in turn:

1. In the first place, the medium affects the energy balance of the reaction and thereby determines to a large extent its «energetic feasibility»; this is expressed quantitatively by the free energy change ΔG of the reaction.
2. It will be seen that this energy balance is related closely to the distance of the two molecules during ET; this distance can be estimated if the distribution of the molecules in space is known, and here again the role of the medium in determining this distribution must be considered.
3. Although a favourable energy balance is obviously a prerequisite for efficient ET ($\Delta G \leqslant 0$), the kinetics of the reaction are equally important. Here again the medium can have a strong influence on the reaction rate constant, specifically on the free energy of activation $\Delta G^{\neq}$.
4. Finally, the question of the separation of ions formed through ET must also make reference to the effect of the solvent. The primary ET process itself takes places mostly between molecules in close contact,

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and free ions will be formed only in certain specific conditions which are related to solvent properties in particular.

In all these cases the role of solvent *polarity* will essentially be considered; this is not to imply that solvent viscosity and relaxation dynamics are unimportant, but it is not possible to treat them in any detail in this text.

This paper is not intended to be only a review of the current state of knowledge of the effects of the medium on photoinduced ET processes, but will consider some of the theories and models critically in the light of experimental results; some new suggestions will be made concerning the role of the solvent in the overall energy balance as well as in the activation energy and the rate of charge separation.

2. The Free Energy Change, ΔG

For an isolated molecule in the gas phase, the primary processes of ET are the ionization and the electron capture or attachment. The ionization potential *IP* is defined as the minimal energy required to separate an electron from the molecule M to infinity; likewise the electron affinity *EA* is the smallest energy needed (or released) to attach an electron from infinity to the molecule. In a simple diagram of the orbitals of a molecule shown in Fig. 1 it is immediately obvious that if the molecule is in an electronically excited state (M*) both the *IP* and the *EA* values are decreased by the excitation energy E^*.

The excited molecule can be ionized by removing the excited electron from its π^* orbital; and it can add an electron to the half-filled orbital, which illustrates the fact that an electronically excited molecule is at the same time a stronger oxidizing agent *and* a stronger reducing agent than the ground state species.

From the point of view of the energetics an ET reaction between two molecules can be described formally as the ionization of the donor D followed by the electron capture by the acceptor A. The energy balance is then

$$\Delta E_\infty = IP(\mathrm{D}) - EA(\mathrm{A}) - E^*(\mathrm{D}) \qquad (1)$$

if the donor D for example reacts through its excited state. This equation implies that the partners D* and A are separated at infinity, since the zero energy level used to define both *IP* and *EA* is the energy of an electron at infinity from the molecule.

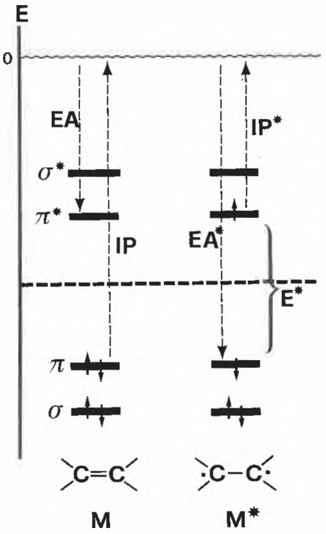


Fig. 1. Orbital diagram of an isolated molecule.

If now D* and A are in fact at a finite distance *r*, then the energy balance must include the electrostatic energy related to bringing the ions together, from infinity:

$$\Delta E_r = \Delta E_\infty + (qq')/r \qquad (2)$$

This electrostatic term is often called the «Coulomb» term, $C = qq'/r$. It is negative for ions of opposite charges and is then a stabilizing term so that the energetics of ET between neutral reactants is increasingly favourable for smaller distances (Fig. 2).

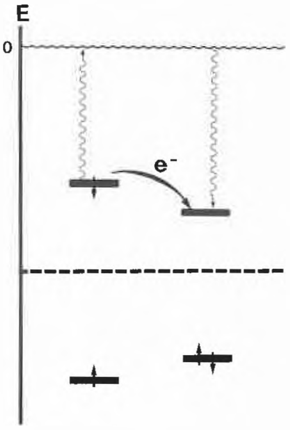


Fig. 2. Orbital diagram for electron transfer between two molecules in vacuum.

Before turning to the ET process in condensed phase, it may be useful to consider briefly the ways in which a solvent reacts to an electric field such as the field of an ion (cf. Fig. 3). The solvent is made up of molecules which are necessarily *polarizable*, that is a small displacement of its electrons and nuclei in the field will produce an induced dipole moment μ_i. This process of *induction polarization* is related to the refractive index *n* of the solvent, specifically to n^2 through a function $f(n^2)$.

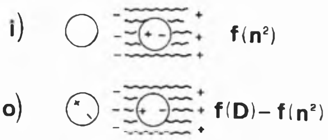


Fig. 3. Response of a solvent molecule to an external electric field: i) induction polarization; o) orientation polarization.

Many solvent molecules possess also a permanent dipole moment μ_s and these form «polar» solvents; in an external electric field the dipoles will tend to lign up with the field, a process of *orientation polarization*. The total dipole moment of the solvent molecule is the sum of μ_i and μ_s, the total solvent polarization being related to the static dielectric constant *D* (or electrical permittivity) through a function $f(D)$. The orientation polarization is therefore related to $[f(D) - f(n^2)]$ which is the difference between the total polarization and the induction polarization[2].

In the liquid phase the ionization of the molecule becomes its oxidation, the electron being given to some electrode of potential E_a instead of empty space; similarly the electron capture is now the reduction, the added electron being drawn from the electrode (Fig. 4). Prior to ET the molecule M is solvated by the medium, and so are the ions after ET so long as the process is reversible.

The energy balance is now

$$\Delta G_\infty = E_{\mathrm{ox}}(\mathrm{D}) - E_{\mathrm{red}}(\mathrm{A}) - E^* \qquad (3)$$

by analogy with Equation (1) for an isolated molecule in the gas phase. In this simple model the oxidation potential E_{ox} is equal to the *IP* of the isolated molecule minus the difference in solvation energy between the starting molecule M and the resulting ion $\mathrm{M}^{\ominus\oplus}$, correction being made for the potential E_a of the electrode with respect to the zero potential of vacuum; and similarly for the reduction process:

$$E_{\mathrm{ox}} = IP - E_{\mathrm{sol.\,ion}} + E_a \qquad (4)$$

$$E_{\mathrm{red}} = EA - E_{\mathrm{sol.\,ion}} + E_a \qquad (5)$$

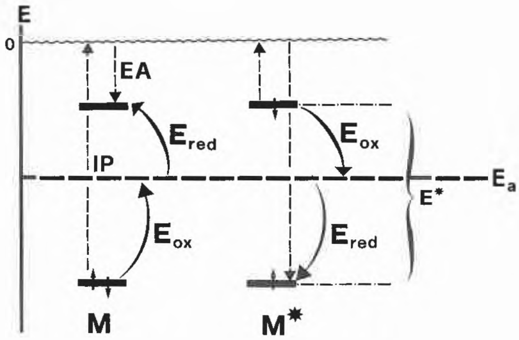


Fig. 4. Orbital diagram of a molecule in a solvent; E_a is the potential of some arbitrary reference electrode.

The effect of the medium appears explicitly for the first time as the solvation energy of an ion. This is given by the «Born equation» which plays such an important role in what follows that it should be discussed briefly:

The Born equation of ion solvation[3] is established very simply by considering the energy required to charge a sphere of radius a to a final electrostatic charge e; if the sphere carries at some time a charge q the repulsive potential against the addition of a further charge dq is $q\,dq/a$ in vacuum, or $q\,dq/aD$ in a solvent of static dielectric constant D. The energies required to charge from 0 to e are then

$$E_{\text{ch. vac.}} = \int_0^e q\,dq/a = e^2/2a \qquad (6)$$

$$E_{\text{ch. solv.}} = \int_0^e q\,dq/aD = e^2/2aD \qquad (7)$$

and the energy difference is the solvation energy, thus

$$E_{\text{sol. ion}} = -e^2/2a(1 - 1/D) \qquad (8)$$

In the case of a non-polar solvent $D = n^2$ since only the induction polarization is operative. For a polar solvent the orientation polarization contribution is therefore

$$E_{\text{orient. pol.}} = -e^2/2a(1/D - 1/n^2) \qquad (9)$$

The important features of the Born equation of ion solvation (Eq. (8)) are the quadratic dependence on the charge (e^2, or in a general way Z^2e^2 for an ion of charge Ze) and the simple reciprocal dependence on the ionic radius ($1/a$). This equation is characteristic of other solvation energy equations in being the product of a factor which depends only on the solute ($e^2/2a$) and one which depends only on the solvent ($1 - 1/D$). This latter factor is therefore a quantitative measurement of «solvent polarity», for the case of solvation of an ion. This quantity varies between 0 (for vacuum, where $D = 1$) to about 1 for highly polar solvents such as acetonitrile ($D = 37$) or water ($D = 80$).

It may be mentioned here that criticism has often been levelled at the Born equation and in particular its derivation in the dielectric continuum model of classical electrostatic[4]. A discussion of these criticisms is beyond the scope of this paper, but the main result of the Born model must be sound since there is no other way to combine a charge and a radius to obtain a quantity which has the physical dimensions of an energy, [charge]^2 [length]$^{-1}$. Returning to the energy balance equation (3) for condensed phase ET, this is valid in principle for two molecules D and A separated at infinity, since the oxidation and reduction steps are independent. As in the case of isolated molecules an electrostatic energy term must be included if the ions are brought to the actual encounter distance r, and this is given as

$$C = qq'/rD \qquad (10)$$

if the ions are point charges separated by the solvent of static dielectric constant D. This Coulomb term of the Rehm-Weller equation [5]

$$\Delta G_r = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) - E^* + qq'/rD \qquad (11)$$

is a stabilizing term for ions of opposite charges, and it favours non-polar solvents ($D \approx 2$) against polar solvents (e.g. $D \approx 80$ for water).

It is no doubt justifiable to treat molecular ions as point charges so long as the centre-to-centre separation r remains large in comparison with their radii a; but when they are in contact there is no more solvent between them and it does not seem logical to keep a screening factor $1/D$.

In a more realistic model the Coulomb term is derived by considering the effective dielectric constant of a system of capacitors connected in series[6], one capacitor being the solute molecules of dielectric constant n_M^2 and the other capacitor being the solvent (Fig. 5).

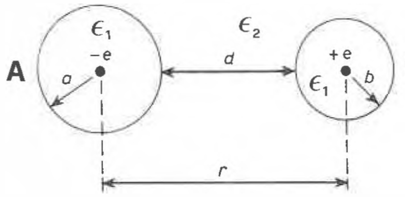


Fig. 5. Model of electrostatic interaction of two molecular ions at short distances.

The general form of the Coulomb term is then

$$C = -e^2\,[a/r^2n_M^2 + (1/rD)\,(1 - a/r)] \qquad (12)$$

For a contact ion pair in a highly polar solvent $D \gg n_M^2$, and since $n_M^2 \approx 2$

$$C \simeq -e^2/2rn_M^2 \simeq -e^2/4r \qquad (13)$$

It is noteworthy that whereas the point charge Coulomb term (10) becomes negligible for highly polar solvents the new formulation $C = -e^2/4r$ is large and amounts for instance to some 0.5 to 1 eV if $r = 6.5$ Å for two molecules in contact. It decreases however rapidly with distance, since as soon as the solvent penetrates between the ions its screening effect becomes important.

According to the new formulation of the Coulomb term some ΔG_r values may be overestimated in the usual form of the Rehm-Weller equation. Indeed, there is some experimental evidence derived from ET reactions in acetonitrile, such as the photoinduced electron capture by p-chloranil[7] and the photoionization of aromatic hydrocarbons[8]:

1. It is observed that the radical anion of p-chloranil is formed from both the lowest singlet and triplet states (Scheme 1). The ET process from acetonitrile appears to be monophotonic and the energy balance based on the values

E_{red} (chl) $= -0.02$ V,

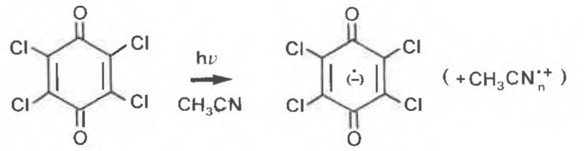
E_{ox}(MeCN) $\simeq 4$ V vs. SCE

implies a Coulomb term $C \simeq 1.2$ eV for $\Delta G = 0$ in the case of the triplet state. Such a large value of C can be understood only on the basis of the very small size of the acetonitrile molecule, and direct contact of the partners is clearly essential.

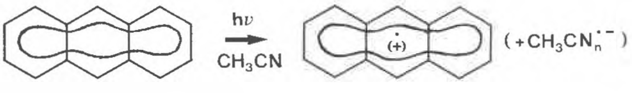
2. Anthracene undergoes the opposite ET process in acetonitrile, namely the photoinduced ionization shown in Scheme 2. This process also appears to be monophonic and takes place from the thermally relaxed singlet excited state S_1. The oxidation potential of anthracene is 0.95 V vs. SCE while the reduction potential of the solvent is -3.5 V vs. SCE; this implies a Coulomb term $C \simeq -0.8$ eV for the energy balance.

These ET processes therefore seem to be energetically feasible only for contact pairs in such highly polar solvents, a small separation being essential for a favourable Coulomb term. In the two cases discussed above van der Waals contact is obviously established at all times since one of the partners is the solvent itself; but in a general sense this raises the question of the distance dependence of ET between partners present in low concentrations. If van der Waals contact is necessary, then this can be obtained through diffusion in dynamic systems such as fluid solvents, or through chance contact or complex formation in static systems such as rigid glasses. In the next section we consider the experimental evidence concerning the distance at which photoinduced ET can take place.

Scheme 1.



Scheme 2.



3. The Distance Dependence of ET

The distance at which electron transfer can take place between two molecules D and A depends on a number of factors: the free energy change of the reaction, the relative orientation of the molecules, and in the case of a photoinduced process on the lifetime of the excited state involved. Ideally one would like to obtain a function of the rate constant of ET versus distance, and for this several approaches can be considered:

1. In a diffusional system such as a fluid solution of D and A the observed rate ET could exceed the diffusional limit if ET can take place at distances greater than the van der Waals radii (Fig. 6).

2. In rigid systems such as a glass or a polymer in which the molecules are dispersed at random it is possible to determine the radius of the effective «quenching sphere» around the excited molecules, e.g. D*.

Since quenching of D* by ET must in this case be static, a simple model implies that if one or more quencher molecules (A) are found within a distance *d* the excited molecule D* will be quenched «instantly», whereas no quenching at all will take place if no molecule A is found within the sphere of radius *d*. This model of static quenching is known as the Perrin model[9], and it applies in principle so long as the rate constant of ET decreases very rapidly with distance (e.g. exponentially) so that the boundary of the quenching sphere is fairly sharp.

3. If the molecules D and A can be organized in some well defined pattern in space it may be possible to vary their distance and thereby to obtain information about the rate of quenching of D* by ET for various separations of the quencher A. Monomolecular layers provide in principle the type of organized assembly required for such measurements[10].

4. The systems considered so far are intermolecular in nature, the donor D and the acceptor A being independent molecules. Intramolecular electron transfer also provides an approach to study the distance dependence, D and A being linked covalently by a saturated chain (e.g. methylene groups $-CH_2-$); they are not distinct molecules any more, but chromophores within a larger molecule (Fig. 7).

A complication does arise in this case, and this was not fully recognized until recently: In an intermolecular ET the interaction is necessarily «through space» but when the A and D chromophores are linked by covalent bonds the possibility of a «through bond» ET cannot be ignored.

5. Finally, it is well known that charge transfer (CT) takes place in the excited states of some conjugated molecules, e.g. 4-nitroaniline[11].

This CT is however only partial, since some overlap must exist between the D and A orbitals for the transition to be allowed; it does not come within the scope of ET considered here, with the one exception of the «twisted intramolecular charge transfer» states (TICT states) of some special molecules which will be discussed further on.

3.1. Luminescence Quenching by ET in Rigid Glasses

It is well established that the photoexcited complex $[Ru(bpy)_3]^{2\oplus}$ is quenched through electron transfer by methylviologen ($MV^{2\oplus}$) in fluid solution. When these molecules are co-dissolved in glycerol and the solution is frozen to form a glass, the quenching of the luminescence of $[Ru(bpy)_3]^{2\oplus}$ is still observed provided the $MV^{2\oplus}$ concentration is high enough[12]. In these conditions the quenching must be static so that the distance at which ET occurs can be estimated according to a modified Perrin model shown in Fig. 8[13].

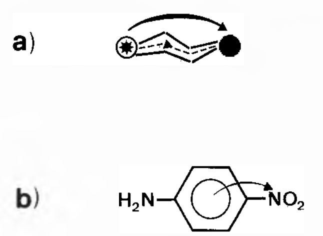


Fig. 7. Models of intramolecular electron transfer a) in a formally non-conjugated bichromophoric molecule, b) in a conjugated molecule.

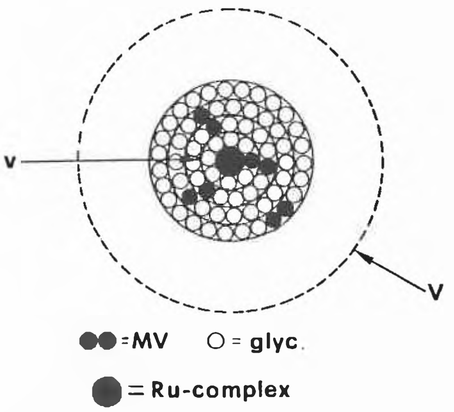


Fig. 8. Discrete site model of ET quenching in a rigid medium.

The modification which is introduced here is that of *discrete* solvent sites around the Ru-complex, so that the edge-to-edge distance between emitter and quencher is not treated as a continuous variable but is allowed to vary only by increments of the molecular diameter of the solvent which also defines the size of each «site». If the Ru-complex is placed at the centre of a sphere of volume V (e.g. 10^3 sites), the sites in which the quencher molecule can be active represent a volume v (the volume of the quenching sphere). When the first quencher molecule is placed at random within the volume V, the probability to find it outside the quenching sphere is $p = (V - v)/V$; for n quencher molecules the probability of finding them *all* outside the quenching sphere is then $[(V - v)/V]^n$, so that the probability of finding one quencher at least within the quenching sphere is $1 - (1 - v/V)^n$. Assuming that the luminescence intensity of the Ru-complexes result only from those molecules which have no quencher within the quenching sphere, the law of static quenching is obtained as

$$\ln(I/I^0) = n \ln(1 - v/V) \qquad (14)$$

In the Perrin model the quenching volume v is considered as a continuous variable, but we shall take it as the volume of the first solvation shell (van der Waals contact) or as the volume of the first and second solvation shells, etc. A computer simulation can be used to place n quencher molecules at random in the 10^3 discrete sites; the distance to the nearest quencher then varies with n as shown in Fig. 9.

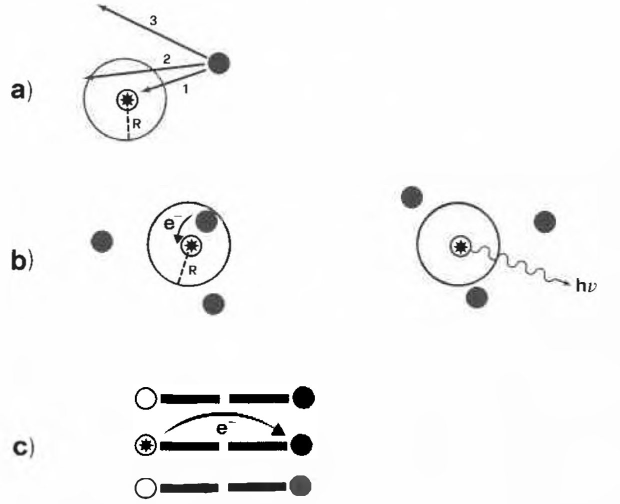


Fig. 6. Models of long-range electron transfer in a fluid (a), a solid (b), and in an organized assembly (c). Excited molecule ⊛, quencher ●, R is the radius of the quenching sphere.

With as few as 10 quencher molecules in 10^3 sites the probability of finding one in van der Waals contact is already over 40%; and for 20 quenchers it exceeds 70%. These values of n (for 10^3 sites) can be converted to molar concentrations and the experimental results can be compared with Eq. (14) taking v as the volume of the first solvation shell, as well as with the data obtained from computer simulations (Table 1).

Table 1. Relative quenching efficiencies of various concentrations of methylviologen ($MV^{2\oplus}$) with $[Ru(bpy)_3]^{2\oplus}$; n = number of $MV^{2\oplus}$ molecules for 10^3 sites in the computer models. (a): Results from Ref.[12]; (b): according to Eq. (14) assuming contact quenching only; (c): computer simulation assuming contact quenching only; (d): computer simulation assuming long-range quenching over one solvent shell; (e): experimental data from Ref.[13].

$[MV^{2\oplus}]$	n	I_n/I_0 (a)	(b)	(c)	(d)	(e)
0.00	0	1.00				
0.05	4	0.86	0.84	0.78	0.43	0.77
0.10	8	0.74	0.72	0.57	0.11	0.58
0.15	12	0.64	0.63	0.47	0.03	0.46
0.20	16	0.55	0.54	0.36	0.01	0.34
0.25	20	0.47	0.47	0.29	0.01	0.26

A good agreement is obtained only if it is assumed that van der Waals contact is necessary for quenching. If electron transfer could take place over a separation of one solvent molecule the quenching slope would be much larger (column (d) of Table 1). This is only one example of the experimental evidence based on quenching through ET in rigid glasses, and the result is that photoinduced ET requires in general the direct contact of the partners. This may be due in part at least to the limited time available for ET in such systems, since quenching must take place within the lifetime of the excited state (ns to µs in these cases). There may be exceptions when the lifetime becomes much longer, of the order of seconds in the case of some triplet states of organic molecules[14]; with such long times strict conditions of static quenching may not always be realized even in glasses which appear rigid according to macroscopic observations, and further work is needed to clarify these situations.

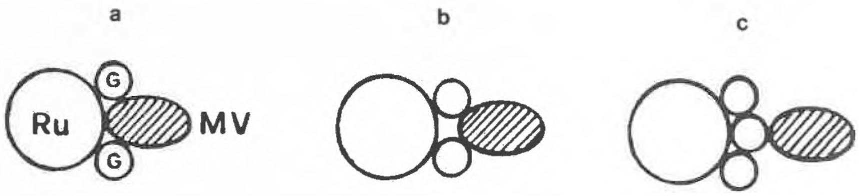


Fig. 10. Models of nearest neighbour molecules in contact (a), separated by one solvent molecule (b), separated by less than one solvent shell (c).

It must be pointed out at this stage that two objections can be made against these conclusions concerning the necessity of direct contact of the molecules for photoinduced ET:

1. In most cases of application of the Perrin model the distance between the molecules is treated as a continuous variable; this could be justified on the basis of situations where the molecules are neither in contact nor separated by a solvent molecule, as in Fig. 10c.

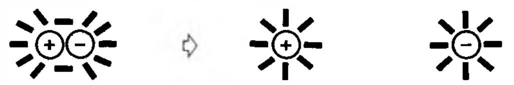
It should however be remembered that liquids (and glasses) are practically incompressible. The volume between the molecules in Fig. 10c would be an «available» volume which would correspond to the compressibility, and it must therefore be concluded that although such situations can exist they are not statistically significant compared to situations such as in Fig. 10a and Fig. 10b. The observed incompressibility of liquids and glasses therefore justifies the use of a model of discrete spacings at short distances, of the order of molecular diameters; as the distance increases this discreteness is gradually lost, but according to the experimental evidence we have to consider only the first few solvent shells as potential sites for ET.

2. The distribution of the quencher molecules around the Ru-complex is assumed to be random, and this is certainly reasonable for neutral species which have no interaction other than that resulting from van der Waals forces. In the present case it must be noted however that both the Ru-complex and the methylviologen quencher carry two positive charges, so that a strong electrostatic repulsion must exist. It is then unrealistic to assume a random distribution for small distances, in particular for the case of direct contact.

This objection appears to be so strong at first sight that it invalidates also the calculations of the quenching sphere radius in the Perrin model using a continuously variable distance; the statistical distribution at short distances can be ruled out[15].

Here it must be pointed out that the equilibrium between paired ions (in contact) and separated ions depends not only on their electrostatic repulsion but also on the solvation energies (Scheme 3).

Scheme 3.



$$E_c = q^2/8a \qquad E'_c = 0$$

$$E_{sol} = -[(2q)^2/(2\sqrt[3]{2}\,a)](1 - 1/D_s) \qquad E'_{sol} = -(2q^2/2a)(1 - 1/D_s)$$

In highly polar solvents $D_s \rightarrow \infty$, and $E \simeq +0.13\,q^2/a$

Applying the Born equation of ion solvation it is readily seen that the paired ion of charge $2q$ and radius $a\sqrt[3]{2}$ is better solvated than the two separate ions of charge q and radius a on account of the quadratic dependence of the solvation energy on the charge. Taking the case of a highly polar solvent it is concluded that the increased solvation energy actually overcomes the Coulomb repulsion; not only is there no net repulsion of ions of the same charge in a polar solvent, but there is on the contrary a driving force for ion pairing, and indeed for the amalgamation of n ions of charge q to form a huge ionic mass of charge nq solvated perfectly in the polar solvent!

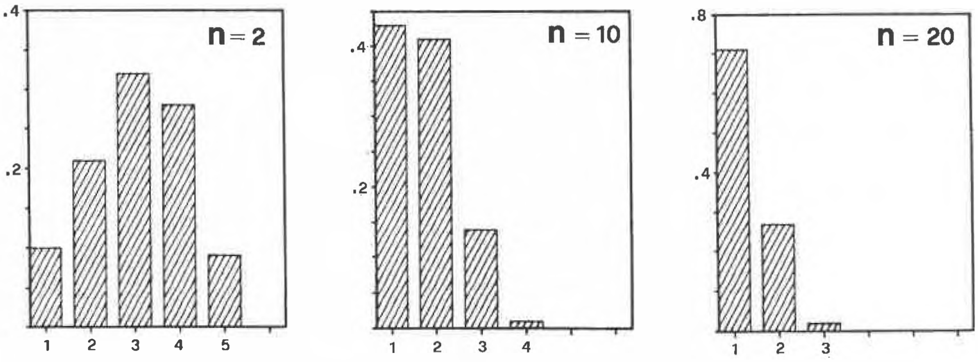
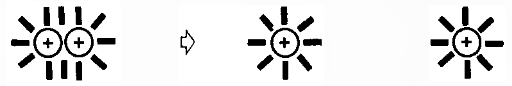


Fig. 9. Computer simulation results of the distance distribution of nearest quenchers to an emitter.

It is however obvious that such a conclusion is absurd and that such amalgamation of ions of the same charge does not occur. The crucial thing which has been omitted in all this discussion is the presence of the counter-ions: Even electrolyte solutions are overall neutral, and in the present case there must be two anions (e.g. $Cl^{\ominus}$) with each Ru-complex and with each methylviologen. The distribution of these counter-ions cannot be ignored, because if they are in contact with the cation the combined supermolecule will be a *neutral* dipole or quadrupole.

The energetics of ion pairing against separation of oppositely charged ions in highly polar solvents is quite straightforward in a simple model, as it turns out that the solvation energies cancel out (Scheme 4).

Scheme 4.



$$E_c = -(e^2/2r)\,(1/n_M^2 + 1/D_s) \qquad E_c' = 0$$

$$E_{sol} = -((er)^2/4a^3)f(D_s) = E_{sol}' = -2(e^2/2a)\,(1-1/D_s)$$

$\downarrow$

in highly polar solvents, $D_s \rightarrow \infty$

According to the Onsager model of a dipole μ of radius r immersed in a solvent of static dielectric constant D, the solvation energy is $(\mu^2/2r^3)f(D)$, where $f(D) = 2(D-1)/(2D+1)$. The ion pair $+q$, $-q$ is equivalent to a dipole $\mu = q \cdot 2a$ and $f(D) \approx 1$ for a highly polar solvent. The radius of the dipole is that of the sphere of the same volume as that of the two ions, $r^3 = 2a^3$; then the energy of solvation of the dipole is q^2/r, and this is exactly twice the solvation energy of an ion of charge q and radius r from the Born equation. If the solvation energies are the same, then the energy balance is determined by the electrostatic interaction term only, $C \simeq q^2/8a$. This suggests that even in polar solvents substantial pairing of cations and anions takes place at high enough concentrations (at low concentrations the adverse entropy term must also be taken into account, as discussed below). When ion pairing is important the cation-anion pairs behave like neutral dipoles or quadrupoles, and their interaction is very weak compared to that of ions so that a statistical distribution can be expected in most cases.

There is indeed some experimental evidence about the association of radical ions with their counter-ions[16], and some molecular dynamics computer simulations give similar results.

4. The Kinetics of ET

Current thinking about the kinetics of ET processes is dominated by the semiclassical model to which the names of *Marcus* and of *Hush* are particularly associated[17]. In its simplest form the rate constant k_{ET} is given by an Arrhenius-Eyring type equation:

$$k_{ET} = \nu_{ET} \exp\left[-\lambda_s(1 + \Delta G/\lambda_s)^2/4RT\right] \quad (15)$$

where the term $\lambda_s(1 + \Delta G/\lambda_s)^2/4$ is similar to the activation free energy $\Delta G^{\neq}$ of the transition state model, ν_{ET} being the frequency of attempted electron transfer and λ_s the reorganization energy. It has been seen above how the solvent affects ΔG, and it intervenes also in λ_s: it is assumed that the solvent must reorganize prior to the ET step (which is much faster than the relaxation of the solvent's orientation polarization) so as to assume the configuration it will have around the species formed in the ET reaction.

Although we are concerned essentially with photoinduced ET processes, it is necessary to discuss briefly the thermal ET reaction known as «self-exchange»; it will indeed be seen that the role of the solvent in the kinetics of ET is clearest in this case.

A self-exchange ET reaction is the transfer of an electron between an ion (e.g. $M^{\oplus}$) and the neutral molecule M:

$$M^{\oplus} + M \rightarrow M + M^{\oplus}$$

The overall free energy is zero in this case, since the chemical system remains in fact unchanged. If $\Delta G = 0$ in Eq. (15), this reduces to

$$k_{ET} = \nu_{ET} \exp(-\lambda_s/4RT) \quad (16)$$

The solvent reorganization energy can now be obtained from the Born equation: It is assumed that the solvent must become unpolarized around the ion $M^{\oplus}$ so as to take the structure it will have around the neutral M; and at the same time the solvent must become polarized around M to reach the configuration in equilibrium with the ion $M^{\oplus}$; then

$$\lambda_s = -e^2\left[1/2a_{M\oplus} + 1/2a_M - 1/r_{MM\oplus}\right] \cdot (1/D - 1/n^2) \quad (17)$$

if r is the center-to-center distance of the partners. The radii a of M and $M^{\oplus}$ can be considered to be identical and for ET between two distant partners ($r \gg a$) the solvent reorganization energy is simply twice the Born orientation polarization energy. The induction polarization is not counted in the reorganization since the induced dipoles in the solvent can follow the ET step. For a contact pair $MM^{\oplus}$ the value of λ_s is halved, as must be intuitively the case when each species is only half surrounded by the solvent.

Recent experimental evidence[18] provides support for the linear correlation between $\lg k_{ET}$ and the solvent polarity function $\gamma = (1/D - 1/n^2)$, as shown in Fig. 11.

However, a considerable quantitative discrepancy appears when a fit is attempted with the value of λ_s calculated from Eq. (17): The line $\lg k_{ET}$ vs. γ is extrapolated to $\gamma = 0$ and the intercept on the $\lg k_{ET}$ axis is then ν_{ET}; a limiting value of k_{ET} is calculated for $\gamma = 1$, taking λ_s from Eq. (17) and it now appears that the slope of the function $\lg k_{ET}$ vs. γ thus predicted is far greater than that observed experimentally.

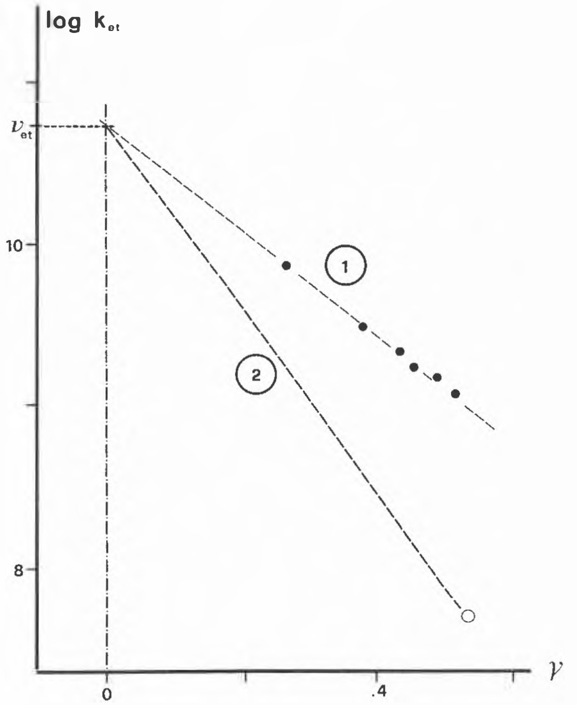


Fig. 11. Variation of the ET rate constant with solvent polarity in a self-exchange reaction; $\gamma = (1/D - 1/n^2)$. ①: Experimental points from Ref. [18]*; ②: calculated line according to Eq. (16) and (17).*

The magnitude of the discrepancy is best noticed from the values of k_{ET} for $\gamma = 1$, 10^9 s^{-1} experimentally but only 5×10^7 s^{-1} calculated. Thus it appears that although the correlation of k with the solvent's orientation polarization is indeed followed in the self-exchange ET reaction, the magnitude of the solvent-imposed activation barrier is very much smaller than the full reorganization implied by the Marcus-Hush theory.

Before considering the possible reasons for this discrepancy, it should be mentioned that in photoinduced ET between neutrals to form an ion pair no such simple correlation with any solvent polarity function is observed[19]. A few examples are given in Table 2, for both inter- and intramolecular processes. In some cases there is a rough correlation with the solvent's refractive index, ET being by and large faster in the more polarizable solvents.

Table 2. Rate constants of electron transfer (k_{ET}) and of quenching (k_q) of various donor-acceptor systems in different solvents. (1): Intramolecular system[19b], k_{ET} in s^{-1}; (2): intramolecular system[20], k_{ET} in s^{-1}; (3): intermolecular system[19c], k_{ET} in s^{-1} M^{-1}; (4): intermolecular system [19a], k_q in s^{-1} M^{-1}: (a): pyrene/*N,N*-dimethylaniline; (b): pyrene/trimethylamine. xEy stands for x · 10^y.

Solvent	D	n	k_{ET} (1)	k_{ET} (2)	k_{ET} (3)	k_q (4) (a)	(b)
C_6H_{12}	2.0	1.42	–	–	–	2.2 E8	1.4 E7
C_6H_6	2.27	1.50	7.3 E8	1.9 E8	1.3 E10	–	–
DIPE	3.55	1.37	–	–	–	9.9 E9	4.4 E9
Et_2O	4.20	1.35	3.7 E8	1.4 E7	–	–	–
$CHCl_3$	4.81	1.45	–	2.3 E9	3.7 E9	–	–
EtOAc	6.02	1.37	6.3 E8	2.1 E7	–	–	–
THF	7.58	1.41	1.3 E9	–	1.1 E10	8.3 E9	6.1 E8
MTHF	7.60	1.41	–	2.0 E7	–	–	–
CH_2Cl_2	9.14	1.42	–	8.1 E8	–	–	–
Me_2CO	20.7	1.36	–	3.0 E7	–	–	–
BuCN	20.3	1.38	–	–	1.3 E10	–	–
PrCN	27.2	1.36	–	5.2 E7	1.1 E10	–	–
MeCN	37.5	1.34	1.6 E8	5.1 E7	1.7 E10	1.0 E10	2.0 E9
DMF	36.7	1.43	–	–	–	5.7 E9	–
Me_2SO	46.7	1.47	–	–	9.5 E9	–	–
n-BuOH	17.5	1.40	–	2.4 E8	–	–	–

DIPE = diisopropyl ether; THF = tetrahydrofuran; MTHF = 2-methyltetrahydrofuran; DMF = *N,N*-dimethylformamide.

The interpretation of these experimental data is not straightforward according to Eq. (16) because the solvent intervenes both in the free energy ΔG and in the reorganization energy λ_s which appear in the exponent. Moreover, the effect of the solvent's polarity is opposite on ΔG and on λ_s: ΔG becomes more favourable in polar solvents as a result of the increasing solvation of the ions, whereas the barrier λ_s becomes higher since more energy is required to reorganize a polar solvent than a nonpolar one.

For these reasons we shall return to the self-exchange ET reaction in which the effect of the solvent on the activation barrier is clear; and we wish now to consider why this barrier may in fact be much smaller than the polarization energy of the solvent.

The basic assumption about the role of the solvent in the Marcus-Hush model is the necessity of its reorganization prior to ET. The energy required for this reorganization has been considered according to the Born equation of ion solvation, but nothing has been said so far about the probability of the solvent reaching of its own accord such a peculiar state of low entropy. On closer scrutiny the sheer improbability of the solvent ever becoming fully polarized around a neutral molecule makes this requirement unrealistic. The only conceivable mechanism for the reorganization as envisaged in the Marcus-Hush model relies on the random fluctuations of the orientations of the solvent molecules, and some experimental evidence concerning the magnitude of such fluctuations will be discussed below; it will be seen that the extensive local reorganization of the solvent shell of a molecule or of an ion appears most unlikely.

In the absence of random solvent reorganization the process of self-exchange can be visualized according to Fig. 12.

The molecule M must come into direct contact with the ion M$^{\oplus}$ for electron transfer; the solvent-imposed activation barrier corresponds then to the disturbance of the polarized solvent shell around M$^{\oplus}$ as M approaches to the distance of van der Waals contact. This disturbance is a partial depolarization of the ion's solvent shell: it is proportional to the solvent polarization energy (linear with γ) but is expected to be much smaller than the total polarization energy. As the neutral molecule M and the ion M$^{\oplus}$ come closer together the electric field of the ion will start to polarize the solvent around M, but this is an energetically downhill process since the ion (MM)$^{\oplus}$ then becomes better solvated. The activation barrier is simply the disturbance of the ion's solvation shell by the approaching neutral.

To sum up, this model of ET considers that there is no solvent reorganization prior to the ET step. Any change in the solvent's orientation polarization must take place at some later time (solvent relaxation).

It is interesting to extend this model of the solvent effect on the rate constant of ET to the reaction between two neutral molecules, e.g. $D^* + A \rightarrow D^{\ominus\oplus} + A^{\ominus\ominus}$. In this model solvent reorganization prior to ET is considered to be so unlikely as to be negligible, and the law of conservation of energy requires that the solvent should retain its orientation polarization during the ET step (on the other hand, its induction polarization can adjust «instantly» to the displacement of the charges). The overall free energy change ΔG takes the full solvent polarization into account, but the ion pair must be formed in an unrelaxed (FC)* state of the solvent; the ΔG(FC) is therefore higher than the final ΔG by the energy of the solvent's orientation polarization E_{op}, as shown in Fig. 13.

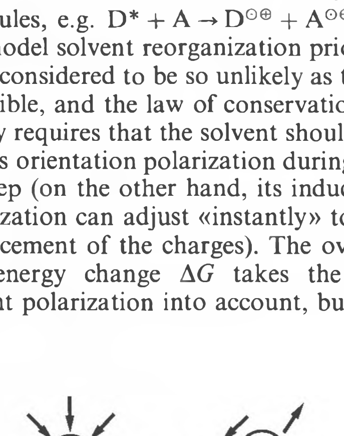


Fig. 12. Solvent polarization effects in a self-exchange ET reaction $M^{\oplus} + M \rightarrow M + M^{\oplus}$.

Some time after the ET step the solvent will relax to reach its final orientation polarization, but the missing E_{op} in the ΔG(FC) which determines the rate constant of the ET process does not necessarily appear as an activation barrier: so long as $\Delta G > E_{op}$ the ET can occur without any solvent-imposed activation barrier. Should such a barrier exist ($E_1 > 0$), then it can be lowered only by the solvent's induction polarization if the solvent is totally unpolarized (orientationally) around the neutral precursors D*A; then the activation barrier will be lower in highly polarizable solvents, that is in solvents of high refractive index (Fig. 14).

This may explain the rough correlation between photoinduced ET rate constants and the solvent's refractive index alluded to above. To all events, this is no more than a rough correlation because the neutral precursors are hardly ever truly nonpolar; their dipole moments will produce some orientation polarization of the surrounding solvent which may (or may not) stabilize the ion pair to some extent.

4.1. Luminescence Quenching by ET in Solution

It has been shown before that in the case of a thermal self-exchange ET process the rate constant k_{ET} decreases with the solvent's orientational polarizability (e.g. the function γ), while in the cases of photoinduced ET listed in Table 2 there is no such correlation; but it must be emphasized that the direct measurement of k_{ET} may not be straightforward and it will be

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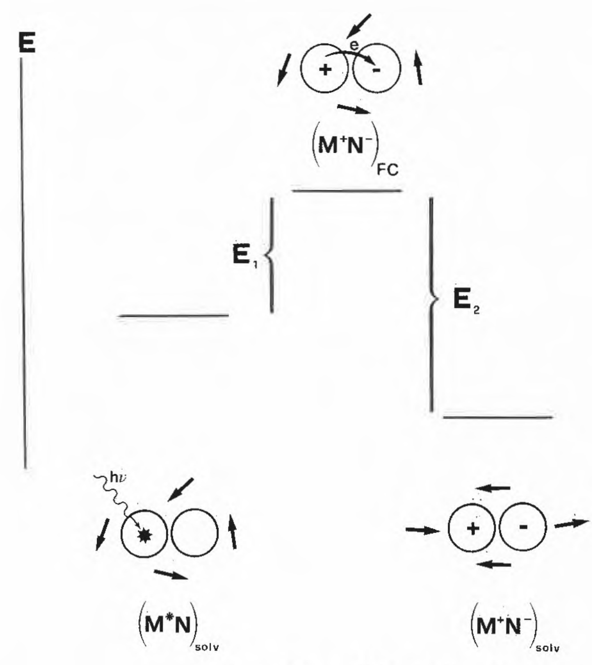
* FC stands for «Franck-Condon», from the names of the scientists who first considered the difference in *electronic* (fast) and *nuclear* (slow) relaxation times of molecules following an electronic transition.



$$E_1 = IP_{M^*} - EA_N + C - E_{ip}$$
$$E_2 = -(\mu^2/2a^3)\,[f(D) - f(n^2)]$$

Fig. 13. Solvent polarization effects in a light-induced ET reaction between two neutral molecules.

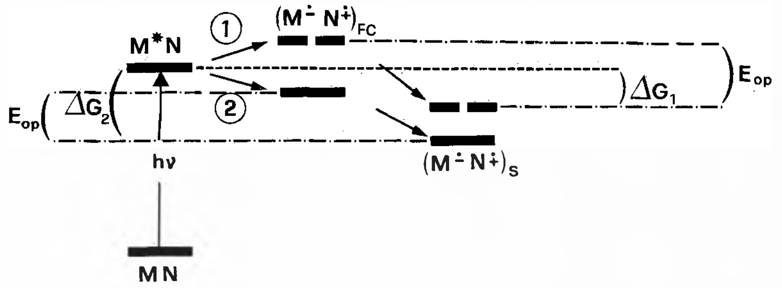


Fig. 14. Energy levels of ET processes: ② without, and ① with a solvent-imposed activation barrier.

shown presently that the solvent effect on the observed rate constant of quenching of excited pyrene by amines for instance may involve some quite different influence of the solvent[19a].

The experimental rate constants of quenching of the fluorescence of pyrene by *N,N*-dimethylaniline and by triethylamine are listed in Table 2, from which it appears immediately that this quenching is relatively inefficient in non-polar cyclohexane but approaches the diffusional limit in highly polar acetonitrile.

There can be no doubt that the quenching process involves ET from the amine to excited pyrene (in its first singlet excited state, S_1); but the correlation of the rate constant of quenching k_q with solvent polarity follows an opposite trend to that of the thermal self-exchange reaction.

This solvent effect can however be understood on the basis of the ET mechanism described above, according to which there can be no solvent reorganization prior to electron transfer. The actual ET step $(M^*N) \rightarrow (M^{\ominus}\ N^{\oplus})$ of rate constant k_{ET} leads to the formation of a FC exciplex or contact ion pair which can subsequently be stabilized by solvent relaxation. In a non-polar solvent there is no stabilization and the contact ion pair $(M^{\ominus}\ N^{\oplus})$ can return to the neutral excited encounter complex (M*N) if the energy difference is small enough (Fig. 15).

In such a case the solvent relaxation leads to irreversibility of the quenching process; but the rate constant of quenching k_q cannot be identified with the rate constant of the ET step itself.

The first step (1) is the diffusional encounter of the excited molecule M* and the ground state molecule N to form an «encounter complex» M*N; electron transfer takes place within this encounter complex (2) to form a contact ion pair in an unrelaxed solvent, assuming that no prior reorganization of the solvent takes place. In a series of solvents of similar refractive index but different static dielectric constants this geminate ion pair may be stabilized by solvent relaxation (3); the solvent-equilibrated ion pair or exciplex can then decay through radiative or non-radiative channels (4) to the dissociative pair of neutral species (5), (6) or it can dissociate into free solvated ions (7). This process of charge separation and ion solvation is discussed further on, but the irreversibility of the ET process itself is determined by step (3), that is by the stabilization of the ion pair or exciplex from its initial non-relaxed (FC) state to the solvated (S) state. In a non-polar solvent there is no such stabilization and the ET process itself may be reversible, depending on the energy gap involved in the forward and reverse ET (2).

In Figure 15 the wriggly arrows of the decay channel (4) are meant to represent both radiative and non-radiative processes other than charge separation; these are shown more explicitly as $h\nu_e$ (exciplex fluorescence) and k_{nr} (exciplex non-radiative recombination) but they apply of course to both FC and solvated exciplexes.

The actual observation is the quenching of the molecular fluorescence $h\nu_f$, and this can be related to the ET process itself (to the rate constant k_{ET}) only if the ET step is practically irreversible, going strongly downhill to the FC geminate ion pair $(M^{\ominus}N^{\oplus})_{FC}$. If this ET step is reversible the quenching of the molecular fluorescence

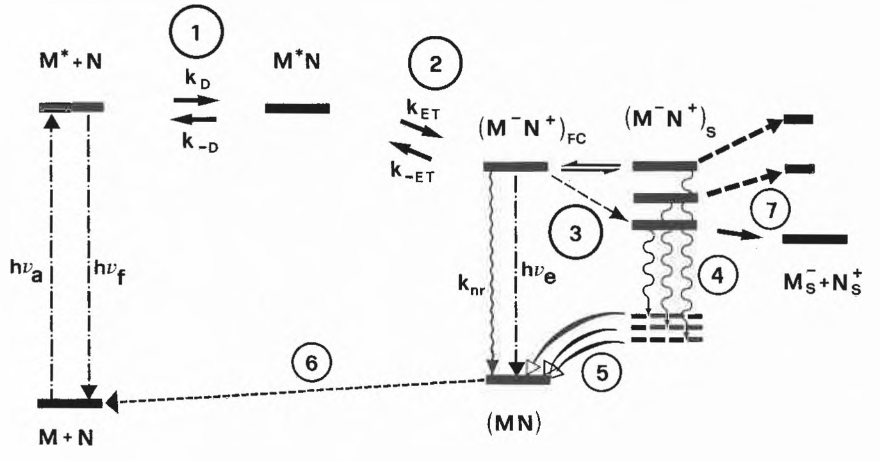


Fig. 15. Energy levels of a light-induced ET reaction through exciplex formation and ionic dissociation.

$h\nu_f$ relies on the further solvation step (3) or even on the charge separation step (7) and it is difficult to relate k_{ET} to solvent polarity. It is however clear that the overall quenching process is at least as efficient in highly polar solvents as in non-polar ones, and this is not expected according to the model of prior solvent reorganization.

4.2. Intramolecular ET between Insulated Chromophores

The most convincing results concerning the distance dependence of intramolecular ET between formally non-conjugated chromophores comes from a recent paper by *Oevering* et al.[19b], in which a series of bichromophoric rigid molecules has been studied.

As seen in Fig. 16, electron transfer takes place between the photoexcited naphthalene moiety and the dicyanoethylene acceptor linked by rigid spacers of varying length. Efficient quenching of the naphthalene fluorescence is observed over center-to-center distances of the order of 15 Å and the rate constant of ET does not follow an exponential decrease with the separation of the chromophores. For this (and other) reasons it is suggested that ET takes place through the bonds of the rigid spacer which acts somewhat like an electron conductor.

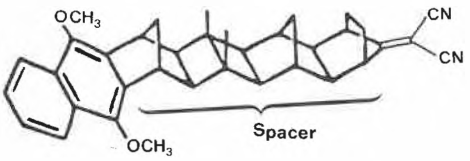


Fig. 16. Outline of a rigid bichromophoric molecule[19b].

The solvent effect on the rate of ET shows again a rough correlation with the solvent's refractive index, benzene in particular being remarkably efficient in promoting this reaction (Table 2).

The rate constant is low in highly polar acetonitrile (which has however a low refractive index), and no quenching is observed in non-polar cyclohexane. This may result from adverse energetics but it is then difficult to understand the high quenching rate constant measured in benzene on the basis of the Marcus-Hush model.

According to these results concerning the through-bond interaction involving a rigid, saturated spacer it has been suggested that the long non-conjugated chains of molecules organized in monolayers may play a similar role in promoting ET over considerable distances; and the phytyl chains of naturally occuring chlorophyll for instance could behave similarly. Although the saturated chains which stabilize the monomolecular structures are not rigid, they are forced into an extended conformation in such ordered assemblies and they may then resemble rigid spacers. The experimental evidence to date is however not at all clear on this point: When a porphyrin is linked to a quinone through a flexible spacer no photoinduced ET seems to take place in the extended conformation; in the folded conformation the donor and acceptor moieties probably come in close contact and quenching by ET occurs[20].

4.3. Experimental Evidence about the Solvent's Local Polarity Fluctuations

It has been mentioned already that in the Marcus-Hush model of ET reorganization of the solvent prior to ET is assumed, and that such reorganization can result only from the local thermal fluctuations of the solvent molecules' orientations around the partner solute molecules. It is therefore important to gain some insight into the magnitude and the frequency of such fluctuations, and one experimental approach relies on the measurement of the solvatochromic shifts of non-polar solutes in polar solvents (the «solvent Stark effect»)[21].

A polar molecule of dipole moment μ and radius a polarizes the solvent in its neighbourhood so that it experiences an electric field $\vec{\varepsilon} = \vec{\mu} a^{-3}\, f(D)$ which is called the reaction field, $f(D)$ being the Onsager polarity function. The solvatochromic shift between two solvents 1 and 2 results from the difference in dipole moments between the ground state (μ_g) and the excited state (μ_e)

$$\Delta E_{1-2} = \vec{\mu}_g \cdot (\vec{\mu}_e - \vec{\mu}_g)\, a^{-3}\, \Delta f(D)_{1-2} \qquad (18)$$

A non-polar solute molecule ($\mu_g = 0$) produces no polarization of the solvent and therefore experiences no reaction field; however, if at any instant of time the solvent molecules should take up orientations similar to that of the polarized solvent around a dipole μ_g an instantaneous electric field $\vec{\varepsilon}$ will exist. This field will induce a dipole moment $\vec{\mu}_{ig} = \alpha_g \vec{\varepsilon}$ if α_g is the solute molecule's polarizability, and this induced dipole will interact with the inducing field to give a stabilization energy.

$$E = \vec{\mu}_{ig} \vec{\varepsilon} = \alpha_g \varepsilon^2 \qquad (19)$$

Although the field $\vec{\varepsilon}$ fluctuates both in magnitude and in direction and its average value is of course zero, the average stabilization energy is finite because it depends on the square of the instantaneous field; the solvatochromic shift now depends on the difference of polarizability between the ground state (α_g) and the excited state (α_e)

$$\Delta E_{1-2} = (\alpha_e - \alpha_g)\, \overline{\varepsilon^2}\, a^{-3}\, \Delta f(D)_{1-2} \qquad (20)$$

where $\overline{\varepsilon^2}$ is the average value of the square of the fluctuating field (Fig. 17).

Solvatochromic shifts linear with $f(D)$ are indeed observed for the first absorption bands of anthracene and tetracene; but there are no shifts for the higher absorption bands which correspond to excitations to increasingly polarizable states. Also, no solvatochromic shift related to $f(D)$ exists for any of the absorption bands of benzene or naphthalene. It therefore appears that the thermal fluctuations of the solvent shell of non-polar molecules are on the whole very small and that large departures from the equilibrium state of solvent polarization are very infrequent. Further work is required in this respect to produce quantitative estimates of the average absolute value of such fluctuating electric fields, and from such data the frequency of fluctuations of the magnitude implied by the model of solvent reorganization may be calculated on the basis of probabilities alone. An explanation for the exceptional solvatochromic shifts of the first absorption bands of some molecules such as anthracene will have to be sought; this is likely to involve the change in the quadrupole moment of these molecules and may have nothing to do with the solvent's local polarity fluctuations. To all events, the more general observation of the absence of solvatochromic effects for non-polar solutes in polar solvents reinforces the assumption that no solvent reorganization can take place prior to ET, at least in light-induced processes which are limited in time by the excited state lifetimes.

4.4. Intermolecular ET in Rigid Media

One example of electron transfer between two molecules codissolved in a rigid glass has been discussed in Section 3.1, namely the quenching of the luminescence

Fig. 17. Principle of the solvent Stark effect; solvatochromic shift of the first absorption band of anthracene in solvents of different dielectric constants.

of $[Ru(bpy)_3]^{2\oplus}$ by methylviologen in glycerol. There are in fact many similar cases which show that ET can be very efficient in polar and non-polar glasses alike, provided a close contact of the partners is obtained by the use of high quencher concentrations[12]. The rate constants of ET can seldom be determined accurately, but an estimate can be made on the basis of the competition between ET quenching and luminescence; since fluorescences of ns lifetimes can be quenched in many cases, it follows that ET rate constants must be of the order of 10^{11} s^{-1}. In a rigid medium solvent reorganization as envisaged in the Marcus-Hush model is of course impossible, at least within the time scale of photoinduced processes in the ns time domain. The efficiency of ET in rigid media is perhaps the strongest piece of evidence concerning the role of the solvent in the kinetics of photoinduced ET: the solvent remains fixed in the reactants' equilibrium configuration, its induction polarization alone being able to follow the motion of the travelling electron.

4.5. Intramolecular ET in Conjugated Molecules; TICT States

Electronic excitation of a molecule is accompanied by a redistribution of its electrical charges. In conjugated molecules this charge transfer (CT) falls short of an actual ET, even though some states have over 80% CT character: for example the first singlet excited state of 4-nitroaniline (a case of intramolecular CT) or the exciplex of anthracene and *N,N*-dimethylaniline (a case of intermolecular CT)[22]. The only well documented case of full ET in an excited state of conjugated molecules is that of the TICT states[23] which result from the loss of conjugation through the twisting at right angle of the donor and acceptor orbitals in molecules such as 4-(*N,N*-dimethylamino)benzonitrile (DMABN; Fig. 18).

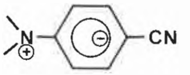


Fig. 18. Intramolecular TICT state of DMABN.

The TICT state is not observable in the absorption spectrum of the ground state molecule because full ET can take place only after electronic excitation to the spectroscopic state S_1 which can relax to the TICT (S_1') state. This relaxation requires the participation of the solvent which must stabilize the large TICT dipole to bring S_1' below S_1; the rate of the twisting and of the concurrent electron transfer depends essentially on the solvent's viscosity and there seems to be no activation barrier related to the solvent's polarity. The kinetics of TICT state formation is peculiar in that the charge transfer increases gradually as the angle of twist increases; thus solvent reorganization is in this case simultaneous with a *slow* ET, whereas in the Marcus-Hush model it is supposed to precede it and we have seen some evidence that it may actually follow it when ET is fast. The TICT fluorescence is characterized by an unusually large solvatochromic shift, as well as by large thermochromic shifts in single solvents (Fig. 19)[24].

These shifts are readily interpreted according to the Onsager model of dipole solvation and the value of the dipole moment of the molecule in the TICT state can thereby be determined. It comes out to around 20 debye which corresponds to the separation of two full electronic charges over 4 Å, in accord with the model of a TICT state having a positive hole at the NMe_2 group and an electron in the PhCN moiety.

It should be mentioned here that exciplex formation between the molecule DMABN and solvent molecules which contain lone-pair electrons has also been suggested to explain its unusual fluorescence properties[25], in particular the large solvatochromic effect; this possibility has been ruled out by the observation of the TICT emission in 1-fluoropentane since this emission is not observed in non-polar perfluorohexane which contains however many more lone-pair electrons[26].

5. Energetics and Kinetics of Charge Separation

In general the photoinduced ET reaction between two neutral molecules forms a contact ion pair, and these ions may either recombine in the solvent cage or may escape to become free, solvated ions; it is well established that this process of charge separation depends greatly on solvent polarity.

The energy balance must consider both the electrostatic interaction (Coulomb term) and the solvation energies, as seen already in Scheme 4.

It turns out that in a highly polar solvent the solvation energy of the dipole made up of the ion pair in contact is exactly equal to the solvation energy of the two separate ions; this equality does not hold exactly for non-polar solvents, but as a good first approximation the energy balance of charge separation can be equated with the electrostatic interaction energy. This is given by Eq. (13) since there is no screening by the solvent for the *contact* ion pair. The ions of opposite charges are therefore held in a potential well by their electrostatic interaction. In the case of a highly polar solvent this well is rather narrow, since as soon as a molecule of solvent comes between the ions the dielectric screening reduces the electrostatic force; on the other hand this screening is much less effective in the case of a non-polar solvent and the ions are still held together at much greater distances. In principle Eq. (12) can be used to calculate the variation of the attraction energy with distance, and Fig. 20 gives a qualitative illustration of the depth and shape of two extreme potential wells.

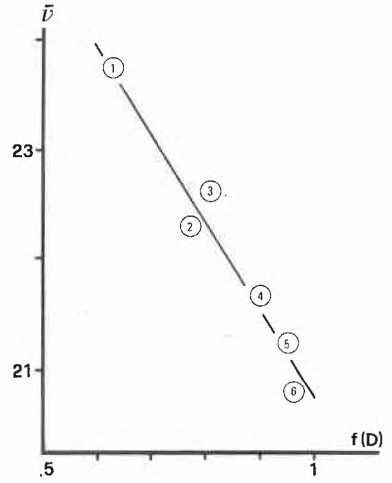


Fig. 19. Solvatochromic shift of the TICT fluorescence of DMABN. Solvents: ① 1-fluoropentane, ② methyl acetate, ③ tetrahydrofuran, ④ 1-butanol, ⑤ acetonitrile, ⑥ N,N-dimethylformamide. f(D): Onsager polarity function $2(D-1)/(2D+1)$; $\bar{\nu}$: transition wavenumber at λ_{max} in 10^3 cm.

The escape of the ions from the cage therefore requires an activation energy which corresponds to the Coulomb term, and this can be quite large even in polar solvents. The temperature-dependence of the free ion yield of some ET reactions in aqueous solution provides some qualitative support for this prediction[27].

It should not be forgotten, however, that the entropy term may be equally important for the separation of any two molecules in contact, since the probability of finding them in the entire available volume V is in general much greater than that of finding them in the contact volume v. The total volume available to any one molecule is related to the concentration, $V = 1/cN_A$ (in liter); the volume restricted to two molecules in contact is $v \approx 32a^3$ if a is the molecular radius, thus the entropy term is approximately

$$\Delta S = -R \ln 32\, c\, a^3 N_A \qquad (21)$$

and this yields for example 30 cal/K for $c = 10^{-6}$ M, that is a value for the energy

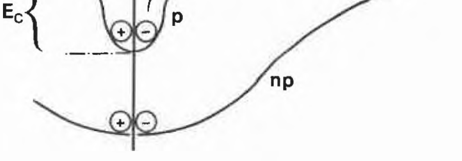


Fig. 20. Model of the potential wells for separation of ions in non-polar (np) and polar (p) solvents.

$T\,\Delta S = 9$ kcal/mol at 300K against a Coulomb term of electrostatic attraction of about 18 kcal/mol from Eq. (13).

The Coulomb term increases with decreasing solvent polarity to reach a value of $C \approx -e^2/2r$ in a non-polar solvent such as a paraffin; this is of the order of 35 kcal/mol and it is not surprising that charge separation is not observed in such conditions.

5.1. Charge Separation in a Non-Relaxed Solvent

The existence of an activation barrier against charge separation assumes that the geminate ion pair is surrounded by a relaxed solvent cage; this ion pair solvation energy balances the free ions' solvation energy and the activation barrier is then the electrostatic attraction. Since is has been argued above that no solvent reorganization takes place prior to electron transfer, two neutral molecules M* and N will in the first place form a geminate ion pair ($M^{\oplus}N^{\ominus}$) in a non-relaxed solvent cage; given time this system will be stabilized by the dipole solvation energy $E_{\mathrm{sol}} = -e^2/a$ if a is the molecular radius (assumed to be the same for M an N). If, however, the time of charge separation is shorter than the solvent relaxation time this dipole solvation energy does not appear in the energy balance, and the charge separation process becomes activationless. There is unfortunately little direct information concerning the rate of charge separation following the ET between two neutral molecules in polar solvents so that it is difficult to say in which cases the charge separation may occur prior to solvent relaxation.

6. Conclusions and Outlook

Although considerable progress has been made in the understanding of ET processes in recent years, several problems remain concerning in particular the effect of the medium:

1. There are hardly any direct measurements of the free energy change ΔG of photoinduced ET reactions. There are of course measurements of the redox potentials and the excited state energies are known from spectroscopic data, but when ΔG is then calculated from the Rehm-Weller equation the result depends on the expression adopted for the Coulomb term. It is therefore highly desirable to have independent experimental measurements of ΔG, for instance through heats of reaction. The experimental problems appear quite serious because of the transient nature of the processes involved, so that conventional calorimetric methods cannot be used; there is however some hope in the development of a technique known as time-resolved photoacoustic calorimetry which is still in its infancy.

2. Many questions remain concerning the distance-dependence of the rate of ET in intermolecular and intramolecular systems. Although van der Waals contact of the partners seems to be the rule for intermolecular ET in the ns-to-ms time scale, there are some exceptions which must be investigated in detail. In the case of rigid media, this «rigidity» needs to be tested for the possibility of microscopic motions at longer times, of the order of seconds.

Intramolecular ET raises some quite different questions: some experiments show that certain rigid saturated spacers can lead to through-bond interaction between distant chromophores, but other experiments suggest that only the folded conformation of chromophores linked by a flexible chain can lead to ET. Such apparent contradictions will have to be resolved, particularly since it is increasingly felt that saturated chains can play an active role in electron transfer in biological systems as well as in man-made organized assemblies.

3. The role of the solvent in the kinetics of ET is likely to remain controversial; in particular the possibility of extensive solvent reorganization prior to the ET step will have to be probed in detail, perhaps with the help of computer simulations to assess the magnitude and the frequency of local solvent polarity fluctuations.

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[1] R. D. Cannon: *Electron Transfer Reactions*, Butterworth, London (1980).

[2] P. Suppan, *J. Chem. Soc. A* (1968) 3125.

[3] M. Born, *Z. Phys. 1* (1920) 45.

[4] P.W. Atkins, A.J. MacDermott, *J. Chem. Educ. 59* (1982) 359.

[5] D. Rehm, A. Weller, *Z. Phys. Chem. (Frankfurt am Main) 69* (1970) 183.

[6] P. Suppan, *J. Chem. Soc. Faraday Trans. 1 82* (1986) 509.

[7] E. Guerry-Butty, E. Haselbach, C. Pasquier, P. Suppan, *Helv. Chim. Acta 68* (1985) 912.

[8] E. Vauthey, E. Haselbach, P. Suppan, *Helv. Chim. Acta 70* (1987) 347.

[9] F. Perrin, *C.R. Acad. Sci, 178* (1924) 1978.

[10] H. Kuhn, *J. Photochem. 10* (1979) 111; D. Möbius, *Acc. Chem. Res. 14* (1981) 63.

[11] P. Suppan, *J. Mol. Spectrosc. 30* (1969) 17.

[12] T. Guarr, M. McGuire, S. Strauch, G. McLendon, *J. Am. Chem. Soc. 105* (1983) 616.

[13] E. Guerry-Butty, PhD Thesis, Université de Fribourg (1987).

[14] J.R. Miller, J.A. Peeples, M.J. Schmitt, G.L. Closs, *J. Am. Chem. Soc. 104* (1982) 6488.

[15] S. Strauch, G. McLendon, M. McGuire, T. Guarr, *J. Phys. Chem. 87* (1983) 3579.

[16] H.L. Friedman, *Faraday Discuss. Chem. Soc. 85* (1988) 1.

[17] B.S. Brunschwig, S. Ehrenson, N. Sutin, *J. Phys. Chem. 91* (1987) 4714, and references contained therein.

[18] G. Grampp, W. Harrer, W. Jaenicke, *J. Chem. Soc. Faraday Trans. 1 83* (1987) 161.

[19] a) P. Jolliet, diplome work, Université de Fribourg (1982); b) H. Oevering, M.N. Paddon-Row, M. Heppener, A.M. Oliver, E. Cotsaris, J.W. Verhoeven, N.S. Hush, *J. Am. Chem. Soc. 109* (1987) 3258; c) J. D. Simon, K.S. Peters, *J. Am. Chem. Soc. 103* (1981) 6403.

[20] a) J.A. Schmidt, A. Siemiarczuk, A.C. Weedon, J.R. Bolton, *J. Am. Chem. Soc. 107* (1985) 6112; b) M.D. Archer, V.P.y Gadzekpo, J.R. Bolton, J.A. Schmidt, A.C. Weedon, *J. Chem. Soc. Faraday Trans. 2 82* (1986) 2305.

[21] N. Ghoneim, P. Suppan, unpublished.

[22] H. Beens, H. Knibbe, A. Weller, *J. Chem. Phys. 47* (1967) 1183.

[23] For a recent review, see W. Rettig, *Angew. Chem. 98* (1986) 969; *Angew. Chem. Int. Ed. Engl. 25* (1986) 971

[24] P. Suppan, *J. Lumin. 33* (1985) 29.

[25] R.J. Visser, C.A.G.O. Varma, *J. Chem. Soc. Faraday Trans. 2 76* (1980) 453.

[26] P. Suppan, *Chem. Phys. Lett. 128* (1986) 160.

[27] M.C. Richoux, *J. Photochem. 22* (1983) 1.

[28] See P. Suppan, *Chimia 42* (1988) 128.