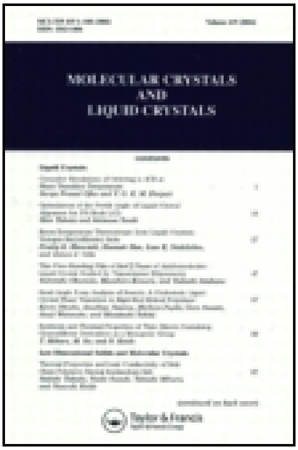

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ON THE CONTROL OF ELECTRON TRANSFER REACTIONS

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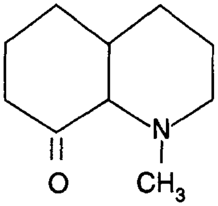
It is the purpose of this note to discuss how to control electron transfer reactions. Such processes are complicated and depend sensitively on the dielectric properties of the solvent medium and the energies and orbital symmetries of the relevant electron states.

To obtain an insight into the process it is therefore necessary to consider simplified models which contain the essential features of the real systems. In the following such a model will be discussed We will assume that donor and acceptor each have two levels and that the donor acceptor system is a rigid structure immersed in a polar solvent charactarized by a local polarization field.

Using such a model it will be argued that by varying Temperature and or external fields it is possible to localize electrons in a controlled fashion.

I.

That the dielectric properties of the solvent can have a major influence on the distribution of electrons in molecules is demonstrated by the molecule:



first studied by Saxena, Stafford and Stafford (1) and also discussed by Griffiths (2).

Solutions of this compound in non polar solvents such as benzene are purple whereas aqueous solutions are orange

As shown by Saxena et al the effect is not chemical and they suggest that in polar solvents an electron transfer from the nitrogen to the Carbon Oxygen double bond takes place.

The charge transfer state is stabilized by interactions with the dielectric medium. Stabilization of a charge transfer states in polar media can be understood in terms of a modified Landau Pekar (3) model of the Polaron applied to a two well system.
To fix ideas consider an H_2^+ molecule.

In vacuum the electron states of this molecule are found by solving the Schrodinger equation:

1) $$E\Psi = \left[\frac{p^2}{2m} - \frac{e^2}{|r-R_{H_1}|} - \frac{e^2}{(r-R_{H_2})}\right]\psi$$

In the simplest LCAO-MD approximation we set:

$$\psi = a\,\varphi_i(r-R_{H_1}) + b\varphi_2(r-R_{H_2})$$

where the φ_ι are appropriate wave functions of the isolated atoms and a and b are variational parameters.

A simple calculation gives a Ground State Energy equal to:

$$E^\circ_H-\Gamma \text{ and } a = b = 1/\sqrt{2}$$

where Γ is the usual coupling constant.

In a polar medium we have to consider the additional interaction energy of the H_2+ molecule with the dielectric solvent.

Following Landau $^{(3)}$ we write the total energy in the form

2) $$\begin{aligned} E = &\int \psi \left(\frac{p^2}{2m} - \frac{e^2}{|r-R_{H_1}|} - \frac{e^2}{(r-R_{H_2})}\right)\psi\, d\vec{r}^3 \\ &+ \int \left(\frac{\alpha^2}{2}\overset{\circ}{P}{}^2 + \frac{\beta P^2}{2}\right) dr^3 \\ &- e^2 \int \mathrm{div}\, P^{(r)} \left[\frac{1}{|r-R_{H_1}|} + \frac{1}{|r-R_{H_2}|}\right] d\vec{r}^3 \\ &+ e^2 \int \mathrm{div}\, P^{(r)} \frac{1}{|r-R_H|}\, |\Psi|^2\, d\vec{r}^3 \end{aligned}$$

where P is the Polarization. In the time independent case we minimize the energy with respect to Ψ and P and eliminate P. This leads to the equation:

3)
$$E\psi = \frac{p^2}{2m}\psi - \left(\frac{e^2}{\varepsilon|r-R_{H_1}|} + \frac{e^2}{\varepsilon|r-R_{H_2}|}\right)\psi$$

$$-\left(e^2\frac{(\varepsilon-1)}{\varepsilon}\int\frac{|\psi(r_2)|^2}{|r-r_2|}\right)\psi$$

where $\varepsilon = \frac{1}{\beta}$

assuming again that:

$$\psi = a\,\varphi_i(r-R_{H_1}) + b\varphi_2(r-R_{H_2})$$

where now
$$E_H\psi_{1,2} = \left[\frac{p^2}{2m} - \frac{e^2}{\varepsilon|r-R_{H_{1,2}}|}\right]\psi_{1,2}$$

a variational calculation of the energy gives approximately:

4) $$E = \frac{E^{\circ}{}_H\text{-}\ (a^2+b^2) + 2\Gamma ab - \Lambda(a^4+b^4)}{a^2+b^2}$$

where $\Gamma = \frac{1}{2} E_H\int\varphi_2(r-R_2) + c\cdot c - \frac{e^2}{\varepsilon}\int\varphi_1\ (r-R_1)\quad\frac{1}{(r-R_1)^2}\ \varphi_2\ (r-R_2)d\overset{3}{r}_2 + c\cdot c$

and $\Lambda = \frac{(\varepsilon-1)}{\varepsilon}\ \frac{\int|\varphi_1(r_1)|^2\,|\varphi_2(r_2)|^2\ d\overset{3}{r}_1\ d\overset{3}{r}_2}{|r_1-r_2|}$

From 4 it follows that if $\frac{\Lambda}{2} > \Gamma$ the states

$a=1,\ b=0$ and $b=1, a=0$

have lower energy than the symmetric state

$a=b=1/\sqrt{2}$

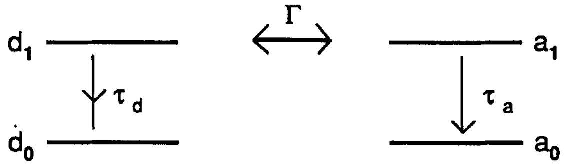
From the previous calculation it follows that the stabilization of the charge transfer state depends on the relative magnitude of the overlap integrals between donor and acceptor states and the electrostatic interaction energy of the complex with the medium.

II.

We now consider a donor acceptor system in which each has two levels

$$E_{d0}, E_{d1}, \text{ and } E_{a0}, E_{a1}$$

We also assume that the states d_0 and a_0 are not coupled and that d_1 and a_1 can decay into d_0 and a_0 respectively. The coupling between d_1 and a_1 will be denoted by Γ and the lifetimes of d_1, and a_1 will be assumed to be τ_d and τ_a the model is summarized below:



We assume that $E_{d1} \approx E_{a1}$ and $KT \ll E_{a1}$

If we now excite an electron from d_0 to d_1 it will "oscillate" between d_1 and a_1 and eventually decay into either d_0 or a_0.

We assume that the oscillation between the excited states can be described by a probability amplitude (Green Function) which obeys the equation:

$$5)\quad \frac{h}{i}\,\frac{\delta}{\delta\tau}\begin{bmatrix} G_{dd} & G_{da} \\ G_{ad} & G_{aa} \end{bmatrix} - \begin{bmatrix} E_{d1} & \Gamma \\ \Gamma & E_{a1} \end{bmatrix} \times \begin{bmatrix} G_{dd} & G_{da} \\ G_{ad} & G_{aa} \end{bmatrix} = I\,\delta$$

If C is the probability that the electron is in the excited state,cd the probability that the electron is on the donor and c_a the probability that the electron is on the acceptor.

$$6)\quad \frac{dC}{dt} = -\frac{1}{\tau_D}\left|G_{dd}^{(t)}\right|^2 C - \frac{1}{\tau_A}\left|G_{dd}^{(t)}\right|^2 C$$

$$\frac{dC_{do}}{dt} = \frac{1}{\tau_D}\left|G_{dd}^{(t)}\right|^2 C$$

$$\frac{dC_a}{dt} = \frac{1}{\tau_a}\left|G_{dd}^{(t)}\right|^2 C$$

If initially the electron is in the state d_1 then for small $\frac{1}{\tau_D}$ and $\frac{1}{\tau_D}$

7) and $$|G_{dd}{}^{(t)}|^2 \approx \frac{1}{2}\left(1 + \frac{\cos 2\Gamma t}{h}\right)$$

$$|G_{dd}{}^{(t)}|^2 \approx \frac{1}{2}\left(1 - \frac{\cos 2\Gamma t}{h}\right)$$

so that:

8) $$\frac{dc}{dt} = -\frac{1}{\tau_d}\frac{1}{2}\left(1 + \frac{\cos 2\Gamma\tau}{h}\right) C$$
$$- \frac{1}{\tau_a}\frac{1}{2}\left(1 - \frac{\cos 2\Gamma\tau}{h}\right) C$$

or 9) $$C = \tilde{c} \exp -\frac{1}{\tau_d}\left(\frac{t + \sin 2\Gamma t}{2\Gamma / h}\right) - \frac{1}{\tau_a}\left(t - \frac{\sin 2\Gamma\tau}{2\Gamma/h}\right)$$

the probability that the electron is in the donor ground state (E_{do}) is therefore approximately:

10) $$C_{do} = \int_0^{\infty} \frac{1}{\tau_D}\frac{1}{2}\left(1 + \frac{\cos 2\Gamma\tau}{h}\right) \exp\left(\frac{-1}{2}\left(\frac{\tau_d = \tau_a}{\tau_d = \tau_a}\right) + \frac{\tau_d - \tau_a}{\Gamma / h \ \tau_d \tau_a} \frac{\sin 2\Gamma\tau}{h}\right)$$

in the limit of large Γ we can neglect the second term and find:

11) $$C_{do} \approx \frac{\tau_a}{\tau_d + \tau_a} + \frac{1}{\tau_D}\left(\frac{\tau_d + \tau_a}{\tau_d \tau_a}\right) \times \frac{1}{\left(\frac{\tau_d + \tau_a}{\tau_d \tau_a}\right)^2 + \frac{\Gamma}{h}{}^{2}_{2}} \approx \frac{\tau_a}{\tau_a + \tau_d}$$

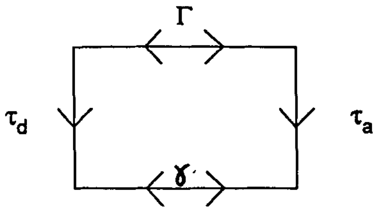
Similarly:

$$C_{ao} \approx \frac{\tau_d}{\tau_a + \tau_d}$$

Hence the transfer depends on the lifetimes of the excited donor and acceptor states to obtain a large yield

$$\frac{\tau_d}{\tau_a} \gg 1$$

Now consider the case where do and ao are weakly coupled



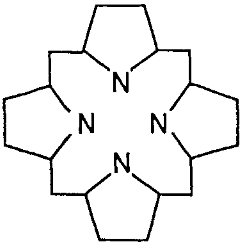
if the system is placed in a dielectric medium such that

$$\gamma < \frac{\Lambda}{2} < \Gamma \quad \text{and} \quad \tau_d \gg \tau_a$$

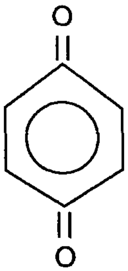
then according to the above D^+A^- will be formed with a reasonable rate.

An example of such a system is provided by the porphyrin quinone system important in Photo Synthesis.

The structures of the two molecules are:

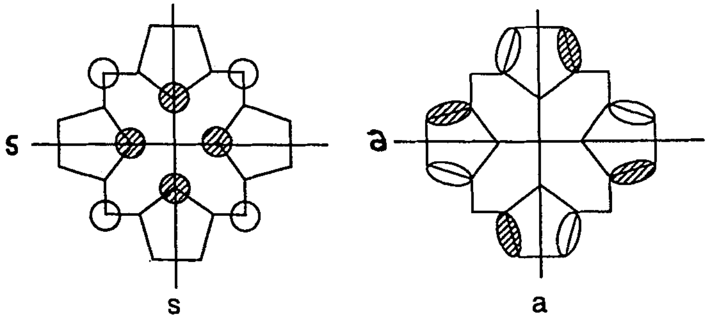


and



As can be seen both molecules have the same axes of symmetry. Using a LCAOMO the highest occupied levels of the porphyrin and quinone can be calculated.

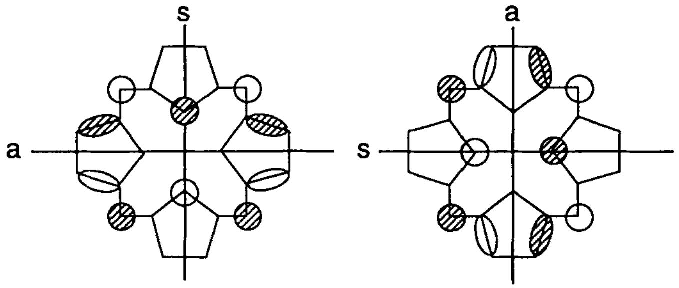
Results of such calculations for the porphyrin are shown below:



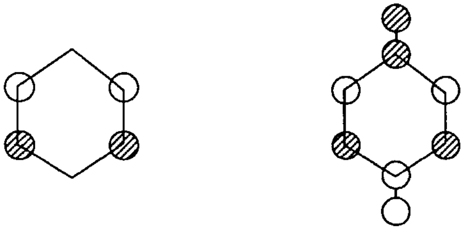
a and s indicate antisymmetric and symmetric states

○ and ▨ refers to the sign.

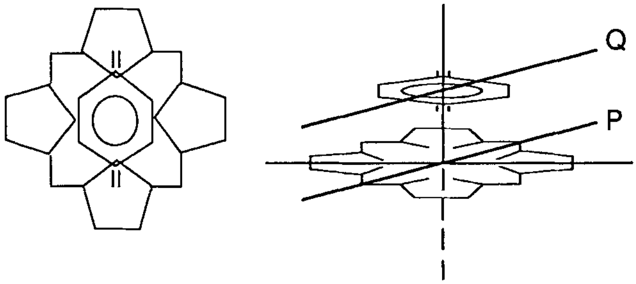
In the same way the first two excited states of the porphyrin can be found. They are:



and the two excited states the quinone are:



as can be seen if porphyrin and quinone are arranged in the for



Then because of symmetry the overlap between one of the excited quinone states and the excited porphyrin states is non vanishing. However the overlap between excited quinone overlap and porphyrin ground state is small. In polar solvents the previous considerations suggest that the charge transfer state might be therefore stable in such a configuration.

III.

Finally consider the question of polarization energy. In the simplest approach to this we can model the solvent as composed by a set of rigid dipoles (a model discussed by Debye [(4)]) in this model the average electric moment of a dipole in a field is given

(in the high temperature limit by

$$12)\quad \overline{m} = \frac{\mu\,|E|}{3\,kT}$$

where E is the electric field and μ the magnitude of the molecular dipole. If we assume that the charge transfer complex acts as a dipole of moment μ_0 then the polarization energy is approximately:

$$13)\quad U \approx \delta\,\frac{\mu^2\,\mu_0^{\,2}}{3\,KT\,Rc^3}$$

where δ is the density (dipoles/volume) of the solvent and R^3 is the "Radius" of the complex. On the other hand the overlap integrals are found to be (4) of the order:

$$14)\quad \varepsilon_0 \quad \varepsilon^{-\alpha R}$$

where in atomic units

$$\varepsilon \approx 0.5 \qquad 0.5 < \alpha < 1$$

and R is the distance between donor and acceptor.

The condition.

$$15)\quad \frac{\delta\,\mu^2 e^2}{R_c 3kT} = \varepsilon_0\,\varepsilon^{-\alpha R}$$

gives:

$$15a)\quad kT = \frac{\varepsilon^{\alpha R}\,\delta\,\mu^2\,e^{\,2}}{3\varepsilon_0 R_c}$$

as condition for stability; raising or lowering the temperature will therefore yield unstable or stable charge transfer complexes.

Finally, it should be noted that external fields will add to or substract from the field of the transfer complex. Therefore by varying external fields stable or unstable complexes can be obtained in polar media.

SUMMARY:

It is argued that the formation of stable charge transfer complexes can be understood in terms of a "autolocalization" mechanism, which depends on the magnitude of the overlap between relevant donor and acceptor molecules and can be controlled by changes in temperature and or external fields. To test these ideas experimentally demands the synthesis of very specific molecular system adapted to the solvent medium.

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