EXCIPLEX AND RADICAL PAIRS IN PHOTOCHEMICAL ELECTRON TRANSFER

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Photo induced electron transfer in polar solvents generates exciplexes and radical pairs. The specific reactions of these intermediates have been studied for systems with pyrene as the primarily excited acceptor and various aromatic and aliphatic amines as electron donors by measuring exciplex decay times and by evaluating time-resolved extinction measurements carried out with and without an external magnetic field of 500 Gauss. The time-independent rate constants thus obtained yield detailed information on electron transfer in general. Their physical significance is discussed.

Photoinduced electron transfer processes between electron donor (D) and acceptor (A) molecules produce in a nanosecond time range high energy intermediates:

exciplexes, (A^-D^+), with an interplanar separation $d \approx 3\overset{\circ}{A}$,

radical pairs, $(^2A^-+{}^2D^+)$, with a center-to-center distance $a \approx 7\overset{\circ}{A}$

and completely separated radical ions, $^2A^-$ and $^2D^+$. These intermediates can undergo subsequent electron back-transfer reactions that lead to either singlet (ground state) or triplet products.

Flash photolytic investigations [1 - 5] carried out in polar solvents have led to the general reaction scheme, presented in Figure 1, which can be interpreted on the basis of the rates of the various single reaction steps involving the intermediates mentioned above.

Fluorescence quenching studies carried out in acetonitrile at room temperature [6] have shown that the electron transfer reaction (1) leading to the radical ion pair

$$^1A^* + {}^1D \longrightarrow {}^1(^2A^- + {}^2D^+) \tag{1}$$
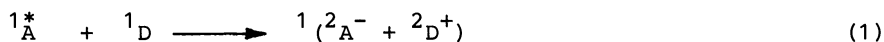
is diffusion-controlled if the free enthalpy gained in reaction (1), is $-\Delta G_1 \geq 0.4$ eV, and remains diffusion-controlled even at very negative values of ΔG_1 where according to the theoretical treatment of electron transfer processes in solution elaborated by Marcus [7] a fall-off in rate by several orders of magnitude is expected. The absence of this fall-off is explained

completely   encounter complex   exciplex
separated species   (a $\approx$ 7Å)   (d $\approx$ 3Å)

$$^1\overset{*}{A} + {}^1D \underset{k_{fid}}{\overset{k_{dif}}{\rightleftharpoons}} {}^1({}^1\overset{*}{A} + {}^1D) \xrightarrow{k_{se}} {}^1(\overset{*}{A} D)$$

$$\downarrow k_{ic}^{exc}$$

$$\Big\downarrow k_{sr} \qquad k_{dis}^{exc} \qquad {}^1(A^-D^+)$$

$$0.75 k_{ass} \quad {}^2A^- + {}^2D^+ \quad 0.25 k_{ass}$$

$$k_{esc} \qquad\qquad k_{esc}$$

$$^3({}^2A^- + {}^2D^+) \xleftarrow{\quad k_{st} \quad} {}^1({}^2A^- + {}^2D^+)$$

$$\Big\downarrow k_{rt} \longrightarrow {}^3\overset{*}{A} + {}^1D \longleftarrow \qquad k_{isc}^{ecx}$$

$$\Big\downarrow k_{rg} \qquad\qquad \frac{1}{\tau_o^{exc}} - k_{isc}^{exc} - k_{dis}^{exc}$$

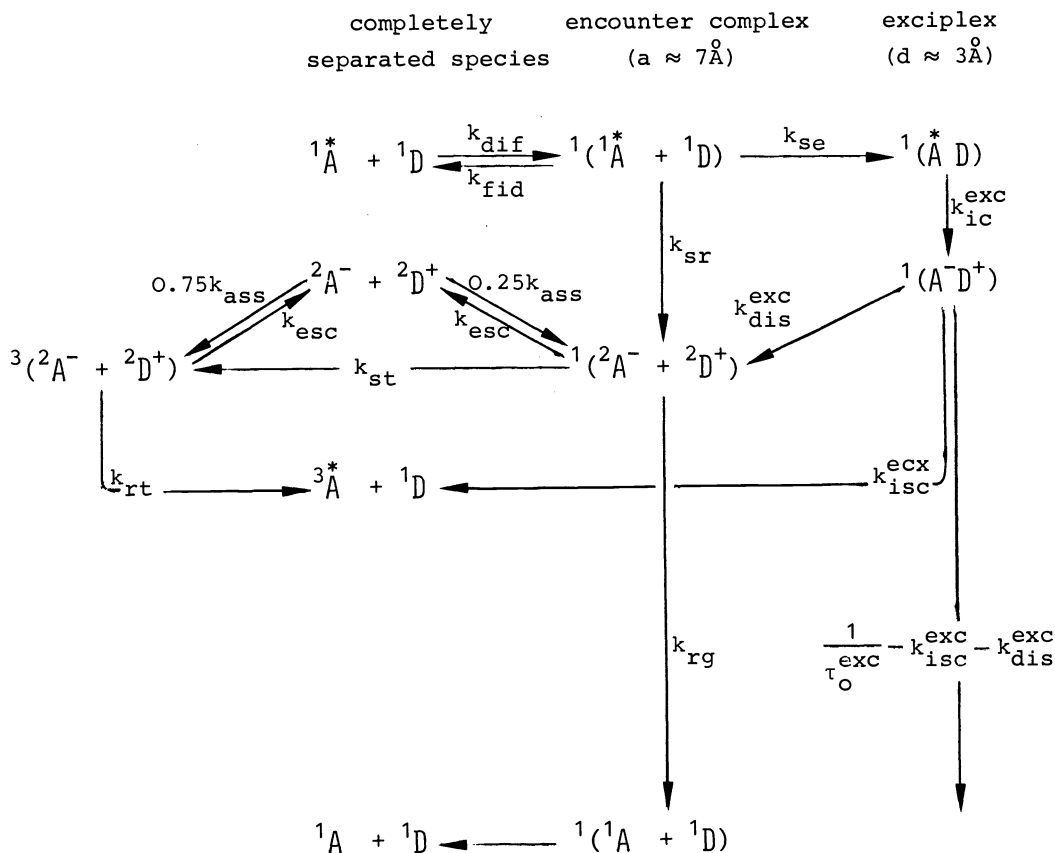$$^1A + {}^1D \longleftarrow\!\!-\!\!-\!\!-\ {}^1({}^1A + {}^1D)$$

Fig. 1 General reaction scheme for photoinduced electron
transfer reactions of electron donor-acceptor systems in
polar solvents. Singlet, doublet, and triplet states are
indicated by left hand side superscripts 1, 2, and 3,
respectively. Lower right hand side indices on the rate
constants stand for: exciplex (e), ground state (g),
radical pair (r), singlet state (s), triplet state (t).

by the assumption that excited exciplex formation (k_{se}) followed by
$k_{ic}^{exc} \geq 10^{12}$ s^{-1} and k_{dis}^{exc} provides another fast electron transfer process
different from k_{sr}.

The rate constant k_{dis}^{exc} of exciplex dissociation into the radical ion
pair

$$^1(A^-D^+) \longrightarrow {}^1({}^2A^- + {}^2D^+) \tag{2}$$
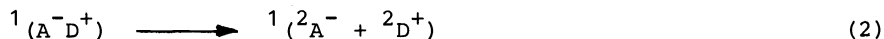
can be obtained from exciplex emission lifetime measurements.
The experimental values determined in polar solvents at room temperature
range from 5×10^8 s^{-1} in acetonitrile to $< 10^6$ s^{-1} in tetrahydrofurane and
agree fairly well with values calculated with the aid of the empirical
equation (3)

$$k_{dis}^{exc}(calc) = \frac{2.3 \times 10^9}{\eta} \text{ [cP} \cdot \text{s}^{-1}] \exp\left(-\frac{e_o^2}{\varepsilon kT}\left(\frac{1}{d} - \frac{1}{a}\right)\right) \tag{3}$$

where η = viscosity (measured in cP), ϵ = dielectric constant of the solvent
used and k = Boltzmann constant [8]. This indicates that exciplex dissoci-
ation (2) leading from the weakly solvated dipolar exciplex to the strongly
solvated radical ion pair requires charge separation against the Coulomb
attraction between the ions as well as diffusional movement of solvent
molecules in the resolvation process.

A detailed nanosecond-flash photolytic investigation carried out in
acetonitrile at room temperature with pyrene as the primarily excited
electron acceptor (A) and several aromatic and aliphatic amines as electron
donors (D) has led to the determination of the pyrene radical anion and
pyrene triplet yields, ϕ_R and ϕ_T, respectively (at 20 ns after laser flash
maximum) that according to

$$\phi_R = \frac{k_{esc}}{k_{esc} + k_{st} + k_{rg}} \qquad (4)$$

and

$$\phi_T = \frac{k_{st}}{k_{esc} + k_{st} + k_{rg}} \qquad (5)$$

depend only on the rate constants of the reactions following formation of
the singlet state radical ion pair. Equations (4) and (5) lead to

$$\frac{k_{rg}}{k_{esc}} = \frac{1 - \phi_R - \phi_T}{\phi_R} \qquad (6)$$

so that with k_{esc} = 0.5 x 10^9 s^{-1} (from magnetic field effect measurement
[9, 10]) k_{rg} values have been obtained ranging from 0.06 x 10^9 s^{-1} for
D = DMA (dimethylaniline) to 12 x 10^9 s^{-1} for D = DABCO (1,4-diazabicyclo-
octane) [8]. This surprisingly strong variation cannot be ascribed to the
small energy gap variation of the systems investigated, but can be qualit-
atively understood on the basis of the following consideration: The
radiationless transition of the π-electron (from the pyrene radical anion)
to the delocalized π-MO of ^{2}DMA$^+$ being only very weakly coupled to
vibrational modes is more or less Franck-Condon forbidden. However, the
transition to the localized lone-pair orbital on the nitrogen atom(s) of
DABCO, which is strongly coupled to the CC-stretching vibrations is Franck-
Condon allowed because the electronic energy can easily be transformed into
vibrational energy of DABCO.

According to the reaction scheme (1) the radical ion pair, $^1(^2A^- + ^2D^+)$,
is initially generated in a singlet electron spin state. Its recombination
by electron back-transfer to give triplet products has been monitored
spectroscopically with a time resolution of about 3 ns and could be resolved
into a fast geminate ($k_{st} \approx 0.06$ x 10^9 s^{-1}) and a slow second order homo-
geneous process. It has been found that both the rate and yield of the
geminate triplet production are reduced by a factor of 1.5 when an external
magnetic field of the order of several hundred Gauss is applied [8]. These
results are in agreement with a theoretical model which is based on the
assumption that the change of spin multiplicity of the radical pair

originates from the hyperfine coupling between the unpaired electron spin
and the nuclear spins within each radical [9, 10]. However, this mechanism
can only be operative if the electron exchange interaction between the
radicals is small compared to the hyperfine interaction, otherwise the
exchange interaction leads to complete damping of the hyperfine coupling
and thus of radical pair triplet formation [10].

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