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UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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COLLEGE ON ATOMIC AND MOLECULAR PHYSICS: PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

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PHOTOINDUCED ELECTRON TRANSFER IN SOLUTION

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PHOTOINDUCED ELECTRON TRANSFER IN SOLUTION

Photoinduced 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.

REACTION SCHEME

of Photoinduced Electron Transfer Processes

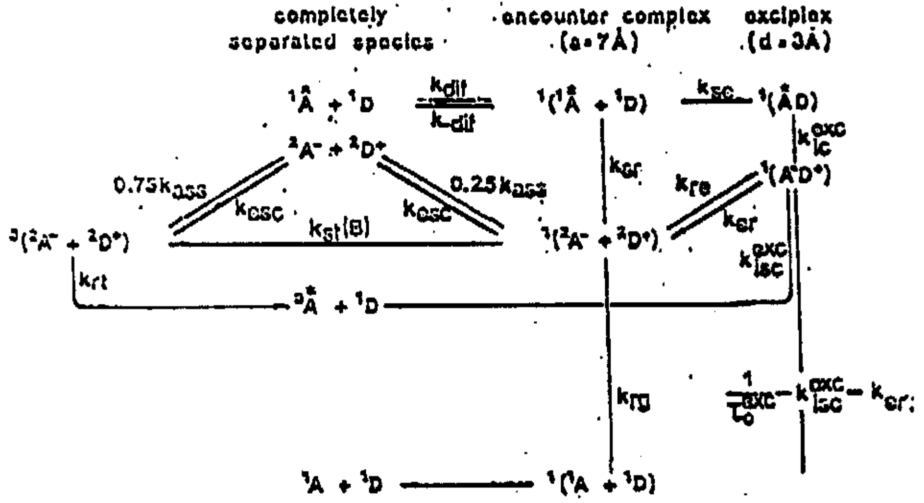
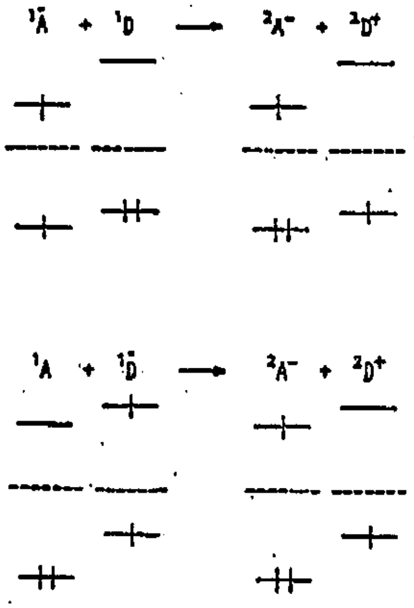
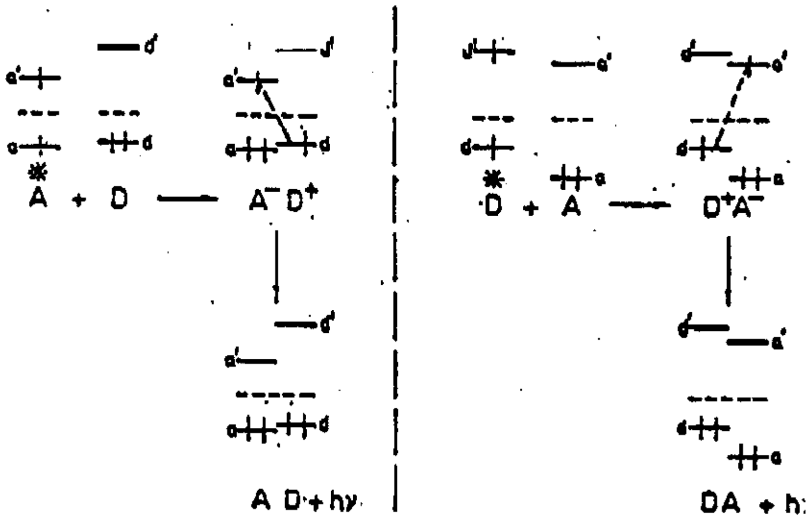
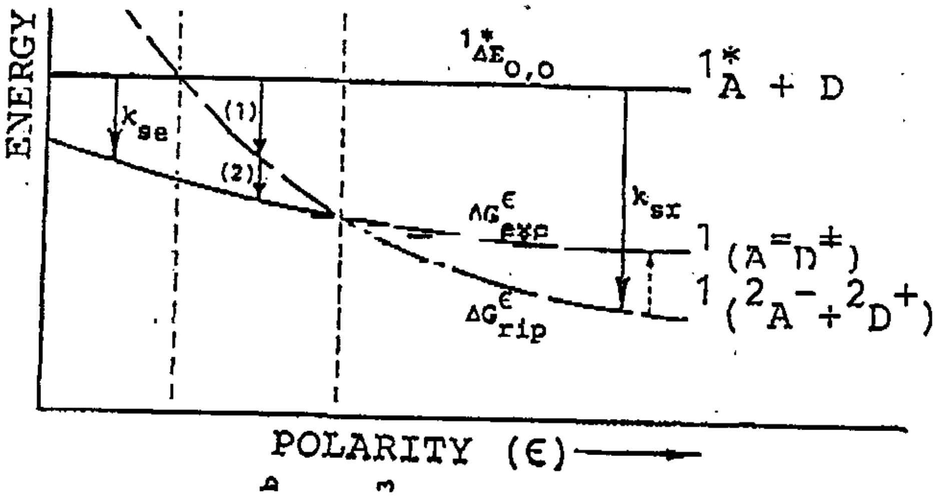


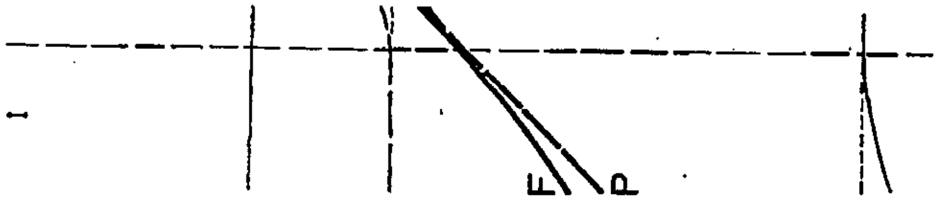
Fig. 1. General reaction scheme for photoinduced electron transfer reactions of electron donor-acceptor systems in polar solvents. Singlet, doublet, and *triplet* states are indicated by left hand side superscripts 1, 2, and 3, respectively. Lower *right* hand side indices on the rate constants stand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

MO-DESCRIPTION OF ELECTRON TRANSFER









Singlet

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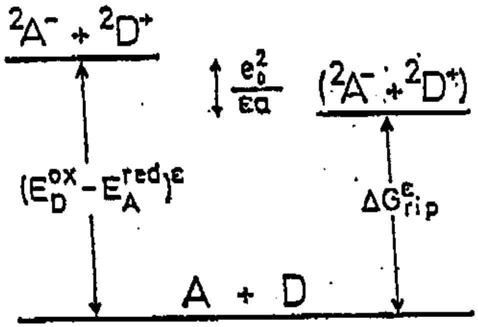
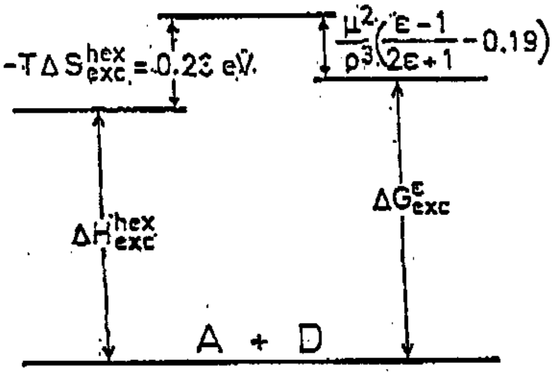


Free energy scheme for radical ion pair formation from completely separated ground state molecules in solvents of dielectric constant ε ($a = 0.65 \pm 0.10$ nm is the assumed center-to-center distance of the solvated radical ions in the pair)

$$\Delta G^{\varepsilon}_{rip} = (E_D^{ox} - E_A^{red})^{37} + \frac{e_0^2}{\varepsilon}\left(\frac{1}{r} - \frac{1}{a}\right) - \frac{e_0^2}{37r}$$

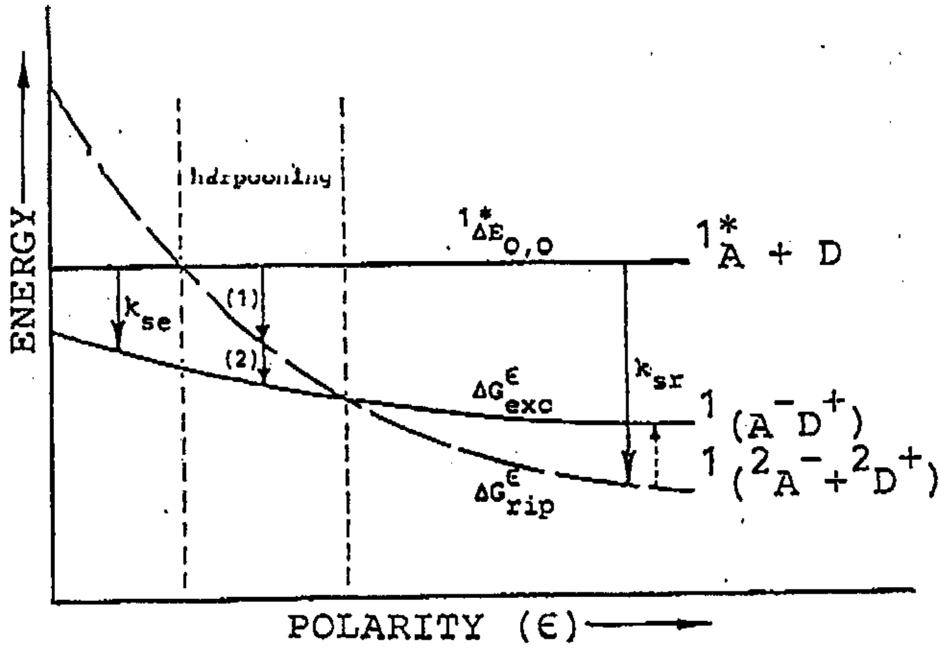
so that with the average values $r_+ = r_- = r = 0.30 \pm 0.03$ nm and $a = 0.65 \pm 0.10$ nm one arrives at the relation

$$\Delta G^{\varepsilon}_{rip} = E_D^{ox} - E_A^{red} + \frac{2.6\,\text{eV}}{\varepsilon} - 0.13\,\text{eV}$$



General energy diagram for the determination of the exciplex formation free enthalpy, $\Delta G^{\varepsilon}_{exc}$ in solvents of dielectric constant ε (for hexane and other saturated hydrocarbon solvents $(\varepsilon-1)/(2\varepsilon+1) \approx 0.19$)

$$\Delta G^{\varepsilon}_{exc} = E_D^{ox} - E_A^{red} + (U_{dest} - U_{stab}) - \frac{\mu^2}{\rho^3}\left(\frac{\varepsilon-1}{2\varepsilon+1} - 0.19\right) + 0.38\,\text{eV}$$



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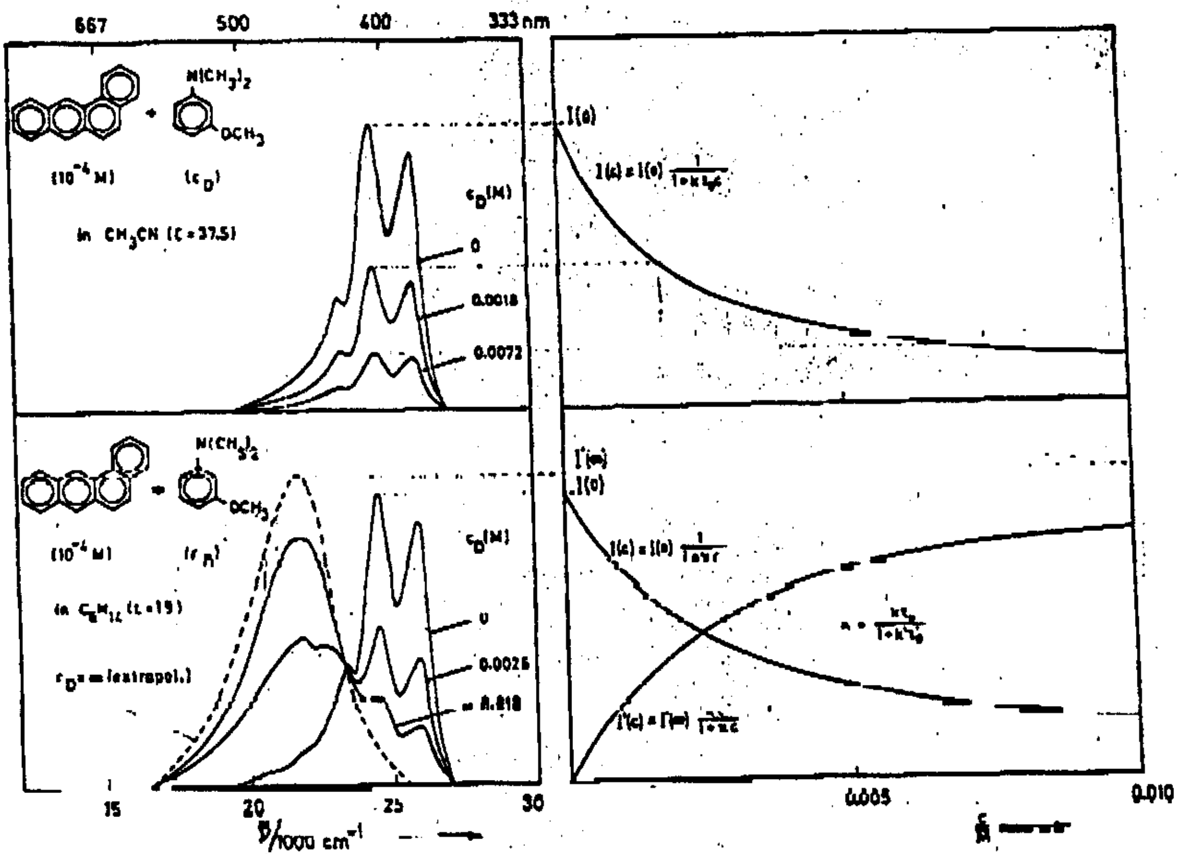

FORMATION FREE ENTHALPIES

of Radical Ion Pairs (rip)		of Exciplexes (exc)
$A + D \xrightleftharpoons{\Delta G^{\epsilon}_{rip}} ({}^2A^- + {}^2D^+)$		$A + D \xrightleftharpoons{\Delta G^{\epsilon}_{exc}} (A^-D^+)$
	as function of SOLVENT polarity (ϵ)	
4.11 eV	hex (1.89)	3.24 eV
3.84 eV	tol (2.34)	3.20 eV
3.33 eV	DEE (4.30)	3.12 eV
3.08 eV	THF (7.30)	3.08 eV
2.86 eV	PrOH (19.7)	3.03 eV
2.80 eV	MeCN (37.5)	3.00 eV
$E^{ox}_D - E^{red}_A + \frac{2.6}{\epsilon} - 0.13$ eV		$E^{ox}_D - E^{red}_A + (U_{dest} - U_{stab}) - \frac{\mu^2}{\rho^3}\left(\frac{\epsilon - 1}{2\epsilon + 1}\right) + 0.52$ eV

A = Py , D = DMA , $E^{ox}_D - E^{red}_A = 2.86$ eV , $U_{dest} - U_{stab} \approx 0$

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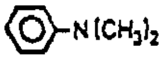
SYSTEMS INVESTIGATED

Electron Acceptors	Electron Donors

$^1\Delta^*E_{0,0}$ = 3.34 eV

$^3\Delta^*E_{0,0}$ = 2.09 eV

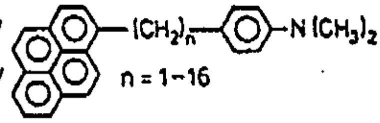


E^{red}_A = −2.10 V vs SCE

E^{ox}_D = 0.76 V vs SCE

$^1\Delta^*E_{0,0}$ = 3.29 eV

$^3\Delta^*E_{0,0}$ = 2.09 eV



E^{red}_A = −2.15 V vs SCE

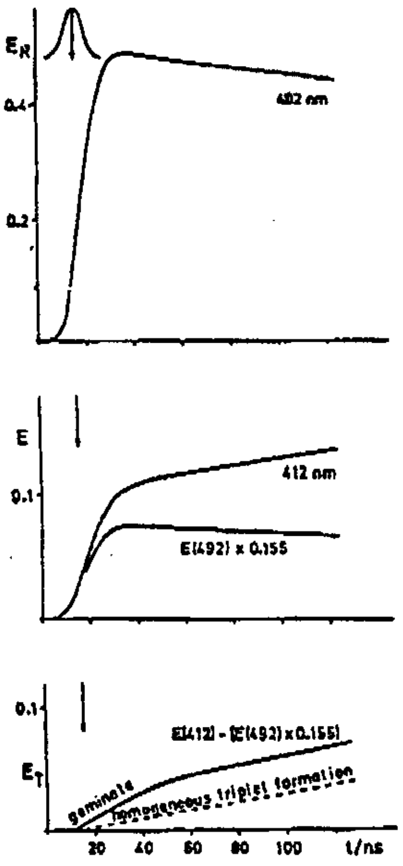
E^{ox}_D = 0.65 V vs SCE

Solvents: Acetonitrile, Methanol, Ethanol, Propanol

Transient absorption of the system pyrene/dimethylaniline in acetonitrile

Top: time evolution of the radical ion extinction

Bottom: time evolution of the pyrene triplet extinction

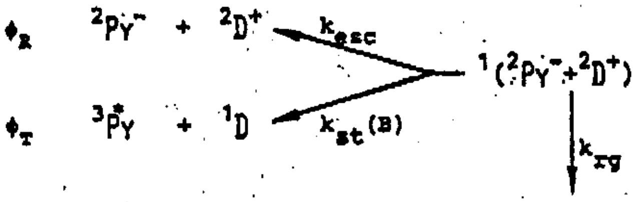


Rate constants of the reaction steps in fig. 1 obtained for the system pyrene (A) + *N,N*-dimethylaniline (D) in acetonitrile at room temperature

	rate constants
k_{dif}	$(20\pm2)\times10^9\ dm^3\,mol^{-1}\,s^{-1}$
k_{sr}	$(40\pm4)\times10^9\ s^{-1}$
k_{or}	$0.49\times10^9\ s^{-1}$
k_{diss}	$(57\pm3)\times10^9\ dm^3\,mol^{-1}\,s^{-1}$ [a]
k_{esc}	$0.5\times10^9\ s^{-1}$
k_{rt}	$(40\pm4)\times10^9\ s^{-1}$
k_{rg}	$0.06\times10^9\ s^{-1}$
$k_{st}(0)$	$0.06\times10^9\ s^{-1}$
$k_{st}(500)$ [b]	$0.04\times10^9\ s^{-1}$

[a] Corresponds to diffusion-controlled rate with 0.7 nm. encounter distance. [b] At external magnetic-field strength ≥500 G.

ELECTRON TRANSFER KINETICS IN ACETONITRILE



$$\frac{k_{st}(B)}{k_{esc}} = \frac{\phi_T}{\phi_R} \quad ; \quad \frac{k_{rg}}{k_{esc}} = \frac{1 - \phi_R - \phi_T}{\phi_R}$$

Donor	Radical Pair Free Energy	ϕ_R	ϕ_T	k_{rg} [a] (s^{-1})
Dimethylaniline	2.80 eV	0.81	0.10	0.06 x 10⁹
3,5-Dimethoxi-dimethylaniline	2.80 eV	0.80	0.10	0.06 x 10⁹
ABCO	3.07 eV	0.34	0.04	0.90 x 10⁹
Triethylamine	3.02 eV	0.30	0.04	1.1 x 10⁹
DABCO	2.61 eV	0.04	<0.01	12. x 10⁹

$k_{st}(0) = 0.06 \times 10^9\ s^{-1}$ and $k_{st}(500) = 0.04 \times 10^9\ s^{-1}$ [a]

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[a] Calculated with $k_{esc} = 0.5 \times 10^9\ s^{-1}$ (obtained from magnetic field effect measurements)