Kinetic and Standard Thermodynamic Parameters of Photoinduced Charge Separation Reactions in a Bichromophoric Anthracene-containing Molecule from Time-resolved Fluorescence Measurements in Different Solvents and Solvent Mixtures and at Different Temperatures

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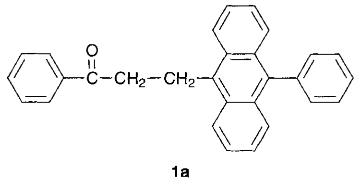
The determination of kinetic and standard thermodynamic parameters (reorganization energies, electronic coupling elements, free energy, enthalpy and entropy changes) of intramolecular photoinduced charge separation reactions in ω-(10-Phenyl-9-anthryl)propiophenone from the analysis of biexponential fluorescence decay curves exhibits distinct differences between the electronic factors in aprotic (benzene, acetonitrile, and mixtures thereof) and protic (methanol, ethanol) solvents and an unexpectedly small variation of the standard free energy change with solvent polarity.

The investigation of photoinduced charge separation (CS) reactions represents a central field of photophysical research, but a systematic study of the solvent dependence of kinetic and standard thermodynamic parameters (rate constants k_{CS}, reorganization energies λ_{CS}, electronic coupling elements V_{CS}, free energy changes ΔG°_{CS}, enthalpy changes ΔH°_{CS}, entropy changes ΔS°_{CS}) of intramolecular CS reactions is still missing. Anthracene and its derivatives are spectroscopically well characterized and thus anthracene moieties are well suited for the elucidation of energy and electron transfer processes in bichromophoric compounds.[1,2]

We have studied the CS reaction of ω-(10-phenyl-9-(anthryl)propiophenone (A–S–P) **1a** in protic (MeOH, EtOH), aprotic (C_6H_6, MeCN) neat solvents and four C_6H_6–MeCN solvent mixtures (M1–M4) at different temperatures with time-resolved fluorescence measurements [using the technique of time-correlated single photon counting (TCSPC), as described before].[3] As an appropriate reference compound we employed 1-(10-phenyl-9-anthryl)-3-phenylpropane (**4b**). Details of nomenclature, syntheses and purification of **1a** and **4b** have been described before.[4]

Singlet and triplet absorption spectra and fluorescence emission and excitation spectra of **1a** and **4b** are in perfect agreement and characteristic for 9,10-disubstituted anthracene derivatives.[4,5] For example, in Fig. 1 a time-resolved fluorescence measurement of **1a** in solvent mixture M2 after excitation of the anthracene moiety (360 nm) is presented. Whereas the reference compound **4b** in all solvents and solvent mixtures under investigation exhibits monoexponential fluorescence decay, the fluorescence decay of **1a** was biexponential, revealing complex deactivation kinetics. We propose that the biexponential fluorescence decay results from the involvement of an ion pair (IP) $^2A^+$–S–$^2P^-$ in the deactivation of the locally excited anthracene moiety in bichromophore **1a** (Fig. 2). The experimental evidence for the participation of an IP is as follows. (*i*) The energetic accessibility of the IP state in MeCN and the consistency (*cf.* Table 1) between ΔG°_{CS} determined from electrochemical measurements (−0.04 eV) and ΔG°_{CS} from time-resolved fluorescence measurements (−0.14 eV). (*ii*) A diminution in all solvents of the short component measured in the fluorescence decay of **1a** (*e.g.* at room temperature, τ_s = 3.4 ns in C_6H_6 and 0.2 ns in EtOH) relative to the fluorescence lifetime of **4b** (*e.g.* τ_F = 8.4 ns in C_6H_6). (*iii*) A strongly monotonic increase of k_{CS} for the CS reactions in the aprotic solvents with increasing solvent polarity (*cf.* Fig. 3). (*iv*) The exclusion of singlet–singlet energy transfer ($^1A^*$–S–P → A–S–$^1P^*$) from negligible spectral overlap of the anthracene fluorescence emission and the phenone absorption spectra, and



1a

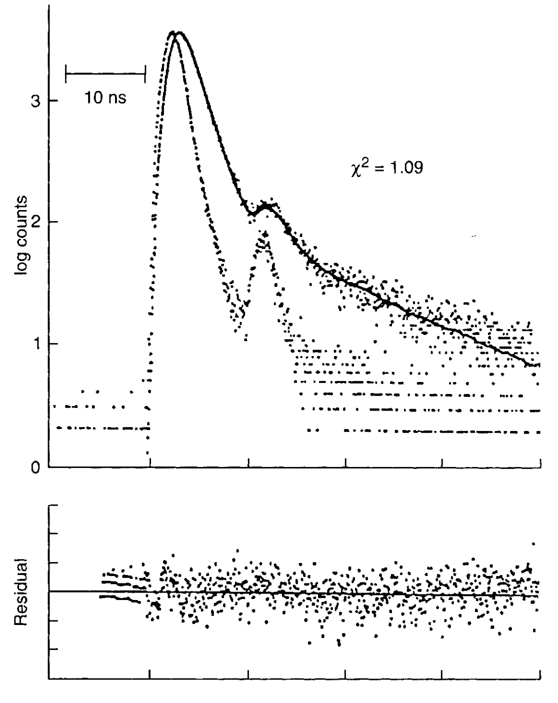


Fig. 1 Fluorescence decay of **1a** in C_6H_6–MeCN mixture M2 (x_{MeCN} = 0.6, ε = 17.1) at 294 K [excitation at 360 nm, detection at 410 nm; residuals from the curve fitting (expressed as weighted deviations) from a fit of a biexponential function are shown below (χ^2: weighted sum of residuals)]

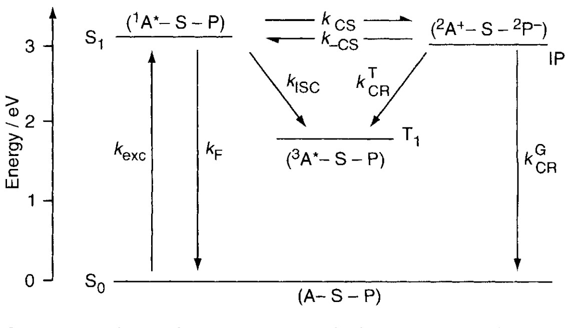


Fig. 2 Energy scheme for the photophysical processes in **1a** [A–S–P: anthracene (A) and phenone (P) chromophores, ethylene spacer (S); rate constants of excitation (k_{exc}), fluorescence (k_F), intersystem crossing (k_{ISC}), forward and reverse charge separation (k_{CS}, k_{-CS}) and charge recombination to triplet and ground state (k^T_{CR}, k^G_{CR})]

of internal conversion[4] ($^1A^*\text{–}S\text{–}P \rightarrow {}^1A\text{–}S\text{–}P$) from the striking solvent dependence of the fluorescence quantum yields of **1a** (Φ_F = 0.34 in C_6H_6 and 0.05 in MeCN). On the contrary, in these solvents Φ_F = 0.75 was found to be constant for **4b**.

Fitting the fluorescence decay curves to the kinetic equations derived from the reaction scheme in Fig. 2 allows the computation of the rate constants of charge separation (k_{CS}), reverse repopulation of the locally excited state (k_{-CS}) and charge recombination to the triplet or singlet ground state (k_{CR}), as exemplarily elaborated by Heitele *et al.*[6]

An Arrhenius analysis of the rate constants k_{CS} and k_{-CS} permits the evaluation of ΔG^o_{CS}, ΔH^o_{CS} and ΔS^o_{CS} from eqns. (1)–(3) (E^A_{CS}, E^A_{-CS} = Arrhenius activation energies; A_{CS}, A_{-CS} = Arrhenius preexponential factors).

$$\Delta G^o_{CS} = -k_B T \ln\left(\frac{k_{CS}}{k_{-CS}}\right) \tag{1}$$

$$\Delta H^o_{CS} = E^A_{CS} - E^A_{-CS} \tag{2}$$

$$\Delta S^o_{CS} = k_B \ln\left(\frac{A_{CS}}{A_{-CS}}\right) \tag{3}$$

An analysis of solvent and temperature dependences of k_{CS} within the framework of Marcus theory for nonadiabatic electron transfer reactions [eqn. (4)], presented in Fig. 3, permits the determination of λ_{CS} amd V_{CS} with ΔG^o_{CS} from eqn. (1) in different solvents and solvent mixtures ($\hbar$ = reduced Planck constant). The application of eqn. (4) is justified since the CS in **1a** takes place in the normal region of electron transfer reactions.

$$k_{CS} = \frac{2\pi}{\hbar} \times \frac{V^2_{CS}}{\sqrt{4\pi\lambda_{CS}k_BT}} \times \exp\left(-\frac{\Delta G^\ddagger_{CS}}{k_BT}\right) \tag{4}$$

$$\text{with } \Delta G^\ddagger_{CS} = (\Delta G^o_{CS} + \lambda_{CS})^2/4\lambda_{CS}$$

Table 1 Kinetic and thermodynamic parameters of **1a** in neat solvents and solvent mixtures from time-resolved fluorescence measurements at different temperatures[a,b]

Solvent (x_{MeCN})	ε	10^{-8} k_{CS} /s^{-1}	λ_{CS} /eV	10^3 V_{CS} /eV	ΔG^o_{CS} /eV	10^2 ΔH^o_{CS} /eV	10^4 ΔS^o_{CS} /eV K^{-1}
C_6H_6	2.3	1.4	1.08	5.9	−0.10	5	5
M1 (0.4)[c]	10.6	3.5	0.91	4.8	−0.10	5	5
M2 (0.6)[c]	17.1	4.1	0.89	4.2	−0.11	2	4
M3 (0.8)[c]	25.4	5.2	0.83	3.4	−0.12	0	4
M4 (0.9)[c]	30.2	5.9	0.86	3.5	−0.13	—[e]	—[e]
MeCN	36.1	7.5	0.85	3.2	−0.14 (−0.04[d])	—[e]	—[e]
EtOH	24.6	55	1.13	30	−0.18	12	10
MeOH	32.7	370[f]	1.24	126	−0.18[f]	17[f]	12[f]

[a] Dielectric constant ε, k_{CS}, ΔG^o_{CS} at 298 K. [b] Estimated uncertainties (from error propagation) are: ⩽ ± 25% for k_{CS}, V_{CS}, ΔH^o_{CS}; ⩽ ± 15% for ΔG^o_{CS}, ΔS^o_{CS}; ⩽ ± 5% for λ_{CS}. [c] Molar fraction of MeCN (x_{MeCN}) given in parentheses. [d] From electrochemical measurements (Weller equation without work term); estimated uncertainty ±0.1 eV. [e] Not evaluated due to unsatisfactory linearity of the Arrhenius plot of k_{CS}. [f] From extrapolated Arrhenius plots (298 K).

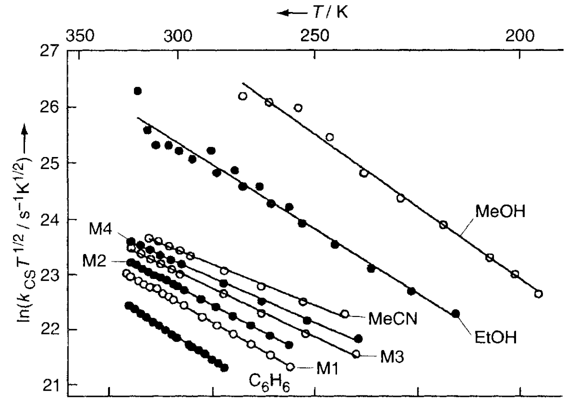


Fig. 3 Marcus analysis of the intramolecular CS reaction in bichromophore **1a** in different neat solvents (C_6H_6, MeCN, MeOH, EtOH) and solvent mixtures (M1–M4)

Table 1 summarizes the kinetic and thermodynamic parameters for the CS reactions of **1a** in the different neat solvents and solvent mixtures. The values of λ_{CS} and V_{CS} for the CS reactions of **1a** in the aprotic solvents (C_6H_6, MeCN, M1–M4) exhibit a small but significant solvent dependence which is clearly documented by the different slopes and intercepts of the lines in Fig. 3 (*e.g.* $\Delta G^\ddagger_{CS}$ = 0.22 eV in C_6H_6 and 0.15 eV in MeCN). Compared to C_6H_6 and MeCN, V_{CS} increases dramatically in the protic solvents (MeOH and EtOH) whereas λ_{CS} varies only slightly.

The free energies, enthalpies and entropies for the CS reaction in **1a** display a small solvent dependence in the aprotic solvents revealing, for example, an increasing exergonicity with increasing solvent polarity (*e.g.* ΔG^o_{CS} = −0.10 eV in C_6H_6 and −0.14 eV in MeCN). Moreover, in protic solvents the CS reaction is slightly more exergonic (ΔG^o_{CS} = − 0.18 eV in MeOH) with enthalpy and entropy terms at least doubled in comparison to aprotic solvents. The variation of the experimentally determined ΔG^o_{CS} values with the dielectric constants of the solvents and solvent mixtures is unexpectedly small and in contrast to continuum–solvent dipole models taking into account macroscopic polarity parameters and refractive indices. Whether this discrepancy may be related to octupolar contributions in C_6H_6 remains an open question.[8,9]

Our experimental results indicate that the increase of k_{CS} from C_6H_6 to MeCN results mainly from an increase in the nuclear (Franck–Condon) factors whereas the increase of k_{CS} from aprotic to protic solvents is due to an increase in the electronic factors. Unusual fast intermolecular CS reactions in biologically relevant systems have been interpreted in terms of electronic coupling enhancement from hydrogen-bonding between donor and acceptor.[10] A hydrogen-bond-supported CS reaction of **1a** in alcoholic solvents may be reflected by the larger enthalpy and entropy changes indicating significantly enhanced solvent reorientation effects compared to aprotic solvents.

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