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# Diffusionless Electron Transfer of Xanthene Dyes in Nonpolar and Weakly Polar Donor- and Acceptor-Solvents

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Diffusionless electron transfer systems, comprised of excited xanthene dyes dissolved in nonpolar or weakly polar electron donor or acceptor, are distinguished by their direct access to the rate constant of electron transfer and by their potentiality for ultrafast electron transfer. We observed short fluorescence lifetimes of ≤ 6 ps for rhodamine 6G dissolved in p-benzoquinone, aniline and N,N-dimethylaniline.

Nonpolar and weakly polar electron transfer systems are extraordinary in regard of their very small reorientation energy, and more important, in regard of the small contribution of rotational solvent dipoles to the overall change of reorientation upon electron transfer. In the absence of solvent dipoles, which limit the rate of adiabatic electron transfer in polar media, nonpolar systems permit electron transfer unlimited by the rotational relaxation time of solvent dipoles. In the extreme of centrosymmetric solvent molecules, the solvent polarization should be completely due to ultrafast nuclear reorientation. To observe such ultrafast electron transfer, a diffusionless system is prerequisite. Diffusionless electron transfer of xanthene dyes dissolved in nonpolar electron donors, like anthracene, had recently been studied by means of relative quantum yield measurements.1) It was shown that these systems have a very small total reorientation energy of about 0.15 eV, dominated by contributions from intramolecular vibrational

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coupling. A steep rise of the rate constant of electron transfer had been observed with decreasing uphill free-energy gap, and the maximum rate constant was found to be about 1/(2 ps). Most of the present weakly polar systems have solvent reorientation energies of about 0.3 eV, in contrast to nonpolar anthracene, which has 0.05 eV only.$^{1)}$ As dyes were used rhodamine 6G (Rh6G), rhodamine B (RhB), rhodamine 101 (Rh101), and pyronine B (PyB), as electron donor-solvents anthracene (AC), aniline (A), and dimethylaniline (DMA), as electron acceptor-solvents p-benzoquinone (BQ), and m-nitrobenzonitrile (NBN), and 1-chloronaphthalene (Clna) as reference system without electron transfer.

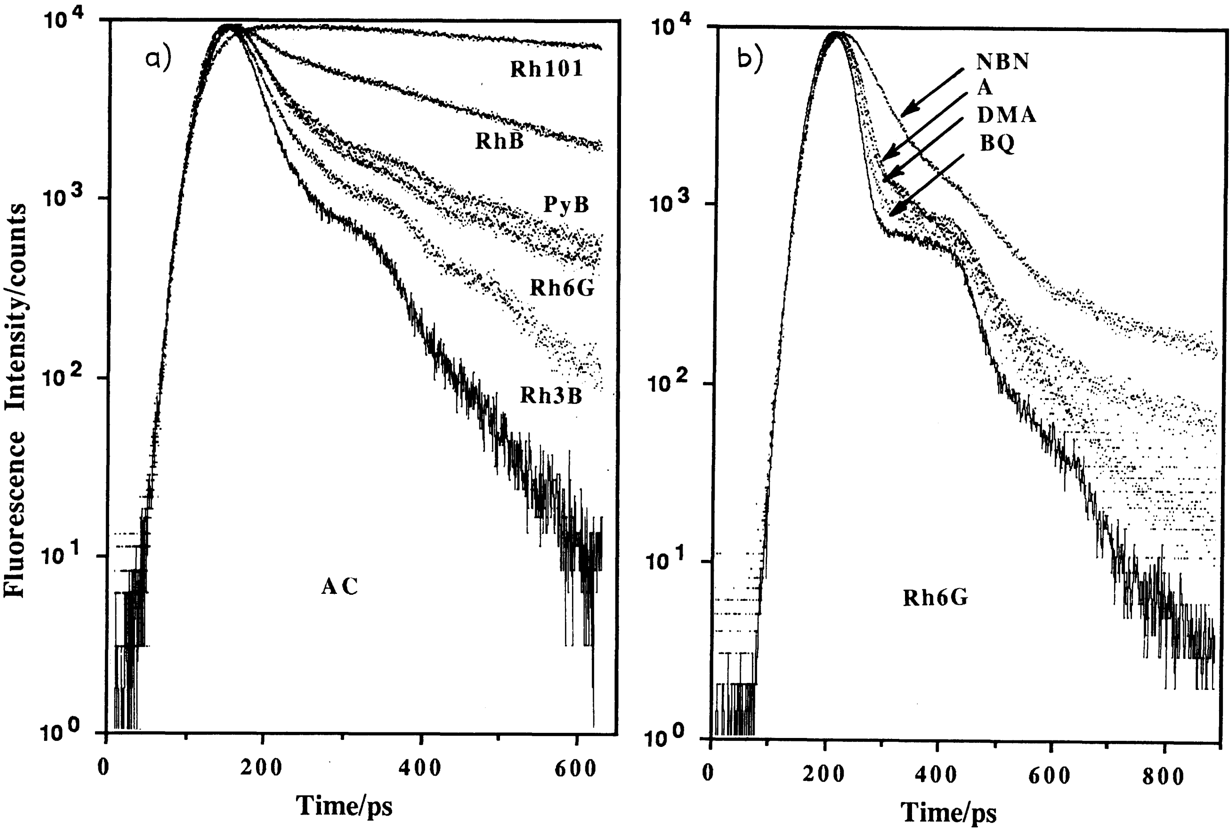

Fig. 1. (a) Fluorescence decays of xanthene dyes in the electron donor anthracene. (b) Rh6G dissolved in the electron donors aniline, and dimethylaniline, and in the electron acceptors p-benzoquinone and m-nitrobenzonitrile. Solid lines indicate system response.

Table 1 shows the analysis of the fluorescence decays of Fig. 1. Table and Figure display fast fluorescence decays of about 6 ps, probably limited by the resolution of the detection system, for Rh6G/A, Rh6G/DMA, and Rh6G/BQ, and relatively slow decays of 50 and 1000 ps for Rh6G/NBN and Rh101/AC, respectively. Short and long lifetimes correspond to a negative or positive free-energy gap, respectively, in Fig. 2.

Table 1. Fluorescence lifetimes and preexponential factors of fluorescence decays in Fig. 1, according to $I(t) = \Sigma_i A_i \exp(-t/\tau_i)$, with i = 1,2,3

| System[a,b] | $\tau_1$/ps | $\tau_2$/ps | $\tau_3$/ps | $A_1$/% | $A_2$/% | $A_3$/% |
|---|---|---|---|---|---|---|
| Rh6G/A | ≤6 | 65 | - | 97.3 | 2.7 | - |
| Rh6G/DMA | ≤8 | 50 | - | 96.6 | 3.4 | - |
| Rh6G/BQ | ≤6 | 80 | - | 99.3 | 0.7 | - |
| Rh6G/NBN | 45 | - | 700 | 99.0 | - | 1.0 |
| Rh6G/AC | 9 | 40 | 500 | 88.6 | 9.4 | 1.9 |
| Rh3B/AC | 18 | - | 200 | 97.7 | - | 2.3 |
| RhB/AC | 28 | - | 350 | 73.6 | - | 26.4 |
| Rh101/AC | 900 | - | - | 100 | - | - |
| PyB/AC | 24 | - | 350 | 94.4 | - | 5.6 |

a) The reference system of 1-chloronaphthalene showed lifetimes of 3.8, 3.7, 3.2, 4.4, and 3.2 ns for Rh6G, Rh3B, RhB, Rh101, and PyB, respectively, at $1\times10^{-5}$ M and 23 °C. b) The measurements were performed by using a time correlated single photon counting system.[2)] The temperature was 23 °C for A and DMA, 125 °C for BQ and NBN, and 230 °for AC. The high temperature and concomitant inherent difficulties of latter system, might be responsible for a relatively large spread of the first lifetime: $\tau_1$ = 9 ± 7 ps for Rh6G/AC.

Table 2. Ionization potential, IP, electron affinity, EA, solvent reorientation energy, $RE_s$, excitation energy, hν, reduction potential, $E_{\frac{1}{2}}$(red), oxidation potential, $E_{\frac{1}{2}}$(ox), and electron affinity of the excited state, $E_{\frac{1}{2}}$(red) + hν

|  | IP[a)] | EA[b)] | $RE_s$ |  | hν[c)] | $E_{\frac{1}{2}}$(red)[d)] | $E_{\frac{1}{2}}$(ox)[e)] | $E_{\frac{1}{2}}$(red)+hν |
|---|---|---|---|---|---|---|---|---|
| AC | 7.13[e)] | - | 0.05[f)] | Rh3B | 2.19 | -0.87 | - | 1.32 |
| A | 7.7[g)] | - | 0.3[h)] | Rh6G | 2.33 | -0.96 | 1.26 | 1.37 |
| DMA | 7.1[g)] | - | 0.3[h)] | RhB | 2.20 | -1.02 | 1.22 | 1.18 |
| BQ | - | 1.9[i)] | - | Rh101 | 2.12 | -1.08 | - | 1.04 |
| NBN | - | 1.56[i)] | 0.3[h)] | PyB | 2.33 | -0.61 | - | 1.62 |

a) All energies in eV. b) Vapour phase. c) In Clna. d) In $H_2O$ vs. SCE (Ref.1). e) In ACN vs. SCE, S.M. Park and A.J. Bard, J. Electroanal. Chem., 77, 137 (1977). f) Ref.1. g) J.L. Franklin et al., Ionization Potentials, 1964,26, NBS. h) Estimated by applying the formula of Marcus, using appropriate radii and solvent parameters.[1)] i) J.V. Beitz and J.R. Miller, J.Chem.Phys., 71, 4579 (1979).

Figure 2 shows the energy relations between the donor-acceptor pairs. The excited xanthene dyes in the centre act as electron donors in combination with BQ and NBN, and as electron acceptors when paired with AC, A, and DMA. Note the large positive energy gap of the reference compound Clna in both $S_0$ and $S_1$, which allows only electron transfer, much slower than the fluorescence decay of the dyes.

The present diffusionless non-polar or weakly polar systems, especially that of dipoleless BQ, are potential candidates for the determination of the ultimate rate of electron transfer and thus the maximal electron exchange matrix element between organic π-donor and π-acceptor in intimate contact.

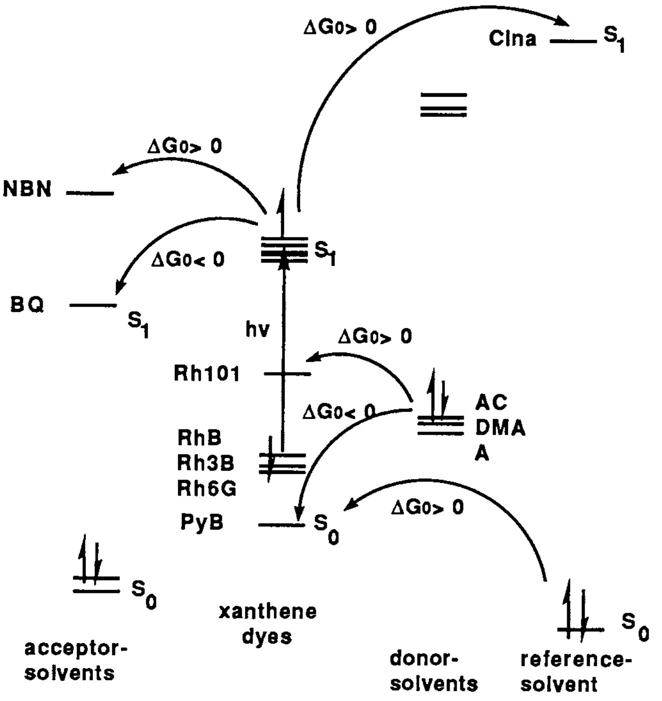

Fig. 2. Relative electronic energy levels of donor-acceptor combinations, as determined by their ionization potentials, electron affinities, and redox potentials (Table 2). The absolute position of the individual energy levels is determined by polarization energies and the electrostatic stabilization energies of the formed ion-pairs.

Femtosecond studies of the related systems of nile blue/A and nile blue/DMA[3] verified the ultrafast character of electron transfer in some of the present nonpolar electron transfer systems.

References

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