Differential Control of Intramolecular Charge Separation and Recombination Rates Using Nematic Liquid Crystal Solvents

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Charge transfer reactions in anisotropic environments are of interest because of their importance in photosynthesis and in the areas of solar energy conversion and optical signal processing.[1−4] Nematic liquid crystals are excellent media for studying intramolecular charge transfer in ordered systems. They are generally good solvents that are transparent at visible wavelengths, permitting the study of donor−acceptor molecules that undergo photoinduced intramolecular charge transfer with visible light. However, there are surprisingly few studies in the literature that explore the mechanisms of charge transfer reactions in liquid crystal solvents.[5−7] The disadvantage of using liquid crystals as anisotropic media is that they possess domains that are highly scattering and, therefore, make optical experiments difficult unless complex alignment techniques are employed. However, it is known that domains with dimensions of tens of molecular lengths persist at temperatures above the nematic to isotropic (N−I) phase transition.[8] This permits the study of charge transfer in anisotropic environments, while eliminating optical scattering, since the molecular domain lengths are smaller than visible wavelengths. We report ultrafast transient absorption studies of an intramolecular donor−acceptor molecule taken above the N−I phase transition of 4′-(*n*-pentyl)-4-cyanobiphenyl (5CB).

The donor−acceptor molecule, PNI−PI, is a 4-(*N*-pyrrolidino)naphthalene-1,8-imide−pyromellitimide[9] that has a rodlike structure. The PI acceptor has a distinctive absorption band at
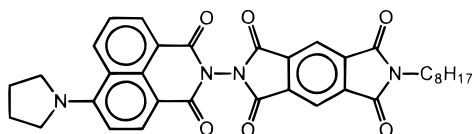
PNI-PI

710 nm when reduced, permitting unambiguous assignment of the final radical ion pair state.[10,11] Time-resolved transient absorption studies were performed with a Ti:sapphire laser system that excited PNI with 400 nm, 120 fs pulses.[12] Transient

absorption kinetics of PNI−PI in 5CB and pyridine, two solvents with similar isotropic static dielectric constants, are shown in Figure 1. The figure clearly shows increased charge separation and recombination times in 5CB relative to those in pyridine. The inset to Figure 1 shows the transient absorption spectrum of PNI−PI in 5CB, which exhibits the characteristic PI⁻ absorption band at 710 nm indicative of the formation of PNI⁺−PI⁻. Figure 2 shows the results of a temperature dependence study of the charge separation and recombination times. The temperature was varied above the N−I phase transition from 310 to 363 K. This figure shows that the charge recombination time constants strongly increase as the N−I phase transition is approached from higher temperatures, while the charge separation time constants increase only weakly.

To analyze this data, we use Landau−deGennes theory which shows that the molecular correlation length $\xi(T)$, is given by the relationship[8]

$$\xi(T) = \xi_0\left[\frac{T^*}{T - T^*}\right]^{1/2} \tag{1}$$

where ξ_o is a molecular length and T^* is just below the N−I phase transition. The N−I phase transition of 5CB containing 2×10^{-3} M PNI−PI was determined to be 306.5 K by differential scanning calorimetry (Perkin-Elmer Pyris 1). We use a value of 306 K for T^*. Equation 1 shows that molecular correlation lengths of approximately 20 exist just above the N−I phase transition and gradually decrease to three molecular lengths at 343 K. From eq 1, the collective reorientation time τ_r of the microdomains has been shown to also change rapidly as the N−I phase transition is approached:[13]

$$\tau_r = \frac{\exp(E_a/k_BT)}{c(T - T^*)} \tag{2}$$

Here c is a constant and E_a is the activation energy for collective reorientation, which has been previously determined to be 34.3 kJ/mol for 5CB.[14] Equation 2 has been shown to be valid for 5CB up to 343 K, where small domain sizes begin to affect the dynamics of the liquid.[13] The data in Figure 2 was fit using eq 2 plus an additive constant τ_{CR}^0 to account for the charge recombination time above the temperature where microdomains exist. E_a and T^* were fixed at 34.3 kJ/mol and 306 K, respectively, and only c and τ_{CR}^0 were varied. The fit to the data begins to err seriously only at temperatures above 343 K where Landau−deGennes theory is known to break down.[13] The identical temperature dependence of the charge recombination kinetics and the collective reorientational dynamics of the microdomains reveals that solvent-controlled reaction dynamics are occurring and that charge recombination is adiabatic.

Although we have shown that the charge recombination times are controlled by the collective reorientation times of 5CB, the charge separation times are certainly not controlled by the same dynamics because no large increase of τ_{CS} is observed as the phase transition is approached. We can interpret the nature of the solvation mechanism for charge separation using the semiclassical Marcus equation for electron transfer:[15]

$$k_{CS} = \frac{2\pi V_{DA}^2 \exp(-\Delta G^*/k_BT)}{\hbar(4\pi\lambda k_BT)^{1/2}} \tag{3}$$

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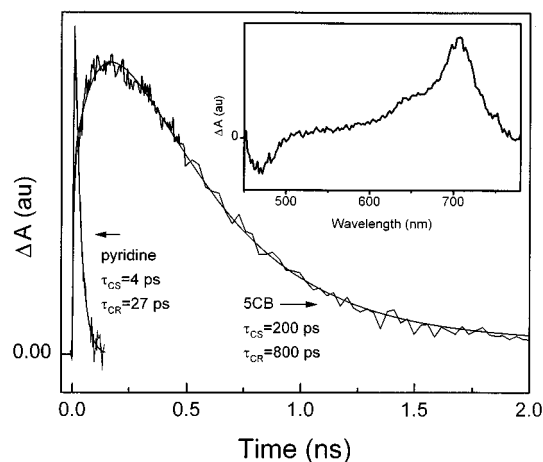(15) Marcus, R. *J. Chem. Phys.* **1965,** *43,* 679.

Figure 1. Transient absorption kinetics for PNI−PI in pyridine and in 5CB at 313 K monitored at 710 nm. The inset shows the transient spectrum of PNI⁺−PI⁻ in 5CB 150 ps after excitation.
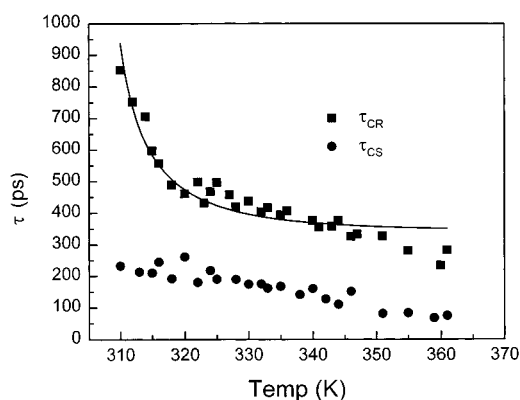

Figure 2. Temperature dependence of the time constants for charge separation (τ_{CS}) and charge recombination (τ_{CR}) for PNI−PI in 5CB are shown.

where $\Delta G^* = (\Delta G^0 + \lambda)^2/4\lambda$, V_{DA} is the electronic coupling matrix element between the donor and the acceptor, ΔG^* is the activation energy for electron transfer, ΔG^0 is the reaction free energy, and λ is the total reorganization energy, which is the sum of reorganization energies due to changes in solvation, λ_S, and internal nuclear coordinates in the donor−acceptor pair, λ_i. Equation 3 assumes that the electron transfer reaction is nonadiabatic, which implies that the solvent motions that mediate charge transfer are fast compared to the rate of charge separation. If eq 3 is obeyed, then a plot of $\ln(k_{CS}T^{1/2})$ *vs* $(1/T)$ should be a line with slope of $-\Delta G^*/k_B$. Using our data for the temperature dependence of the charge separation, such a plot is illustrated in Figure 3 and yields $\Delta G^* = 0.25$ eV. Since the plot in Figure 3 is linear, it is clear that the charge separation reaction remains in the nonadiabatic regime, and thus, the retardation of the charge separation rate in 5CB relative to that of pyridine is a consequence of fast molecular motions that differ from the slower microdomain reorientational responses.

To slow the rate of charge separation, ΔG^0 and/or λ must differ significantly between 5CB and pyridine. Both ΔG^0 and λ depend on the dielectric properties of the medium. For 5CB the isotropic static dielectric constant ϵ_S at temperatures slightly above the N−I transition is 10.5,[16] while that of pyridine is 12.5.[17] However, the rate of charge separation in 5CB is 50 times slower than that observed in pyridine. This suggests that the solvent microenvironment in 5CB at temperatures just above
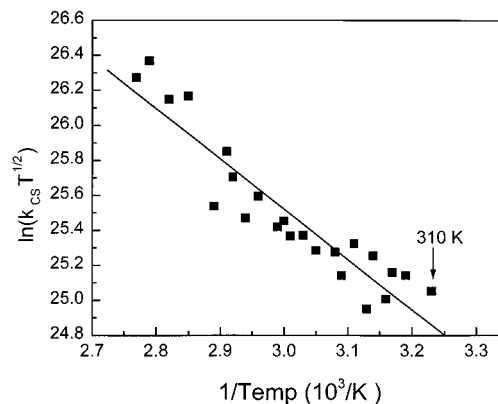
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Figure 3. Plot of $\ln(k_{CS}T^{1/2})$ *vs* $(1/T)$ for charge separation within PNI−PI in 5CB.

the N−I transition does not reflect the isotropic static dielectric constant for the medium.

For charge separation reactions, it has been shown that ΔG^0 becomes more positive and λ_S decreases as ϵ_S decreases.[15,18] For charge separation reactions in continuous dielectrics, ΔG^* can be related to ϵ_S by[19,20]

$$\Delta G^* = \left(\Delta G_E + \lambda_i + \frac{C}{\epsilon_0}\right)^2 \bigg/ 4C\left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_S}\right) \quad (4)$$

where $C = e_0^2[(1/2r_D) + (1/2r_A) - (1/r_{DA})]$ and $\Delta G_E = E_{ox}^D - E_{red}^A - E_S$. In these equations e_0 is the electronic charge, ϵ_0 is the high-frequency dielectric constant of the medium, E_S is the lowest excited singlet state energy of PNI, E_{ox}^D and E_{red}^A are the one-electron oxidation and reduction potentials of PNI and PI, respectively, in polar media, r_D and r_A are the ionic radii of the donor and acceptor, respectively, and r_{DA} is the distance between them. For PNI−PI, $E_S = 2.65$ eV, $E_{ox}^D = 1.09$ V,[21] $E_{red}^A = -0.80$ V,[21] $r_D = r_A = 3.5 \pm 0.5$ Å,[22] and $r_{DA} = 11$ Å.[22] For both 5CB and pyridine $\epsilon_0 \cong 2.3$. Using $\lambda_i = 0.3$ eV[12] and the value of ΔG^* obtained from the data in Figure 3, eq 4 can be solved to obtain an *effective* $\epsilon_S = 6 \pm 3$ for the charge separation reaction in the 5CB microdomains. Since the anisotropic static dielectric constants for 5CB in its nematic phase are approximately $\epsilon_\perp = 6$ and $\epsilon_\parallel = 18$,[16] our results suggest that motions of 5CB perpendicular to its director in the microdomains are sufficiently fast relative to charge separation within PNI−PI to promote rapid, nonadiabatic charge separation. Therefore, the anisotropic dielectric properties of liquid crystal solvents can be used to control the rates and mechanisms of electron transfer reactions. This is an important goal of research focused on the design of efficient photochemical charge separation and storage molecules.

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(22) Ion pair distances were estimated from structures calculated using a modified MM2 force field within Hyperchem (Hypercube, Waterloo, Ontario).