Controlling the Adiabaticity of Electron-Transfer Reactions Using Nematic Liquid-Crystal Solvents

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Transient absorption studies of intramolecular photoinduced charge separation and thermal charge recombination were carried out on a molecule consisting of a 4-(*N*-pyrrolidinyl)naphthalene-1,8-imide donor (PyrNI) covalently attached to a pyromellitimide acceptor (PI) dissolved in the liquid crystal *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA). In the isotropic phase, just above the nematic to isotropic phase transition, ordered microdomains exist that give rise to solvation dynamics that consist of collective reorientational motions of the microdomains and relatively faster reorientations of molecules within the domains. The different temperature dependence of these responses permits the assignment of collective or molecular solvent motions as mediators of the charge separation and recombination reactions. We find for PyrNI−PI in MBBA that charge separation is adiabatic and controlled by the collective microdomain reorientations, whereas the charge recombination is nonadiabatic and controlled by the faster molecular motions within the domains. The data are compared to results for charge separation and recombination within PyrNI−PI dissolved in 4′-pentyl-4-cyanobiphenyl (5CB) under similar conditions. In 5CB, the opposite behavior was observed, i.e., the charge separation is nonadiabatic while the charge recombination is adiabatic. The results are interpreted as arising from the different signs of the dielectric anisotropies of the two liquid crystals, where that of MBBA is negative while that of 5CB is positive.

Recent efforts to understand the effect of anisotropic environments on charge-transfer reactions have employed nematic liquid crystals (LCs) as an orienting solvent.[1−5] The reduced ability of LC solvent molecules to reorient rapidly in the presence of an ion pair, as compared to isotropic solvents, dramatically slows the rates of both charge separation and recombination, which permits the observation of a variety of interesting phenomena. For example, the spin dynamics of the electron-transfer reactions within photosynthetic reaction centers was mimicked for the first time in an electron donor−acceptor model system dissolved in a LC.[6] This was made possible by the fact that the lifetimes of the radical pair intermediates in the LC were sufficiently long to allow their observation by time-resolved EPR.

We now report transient absorption studies of intramolecular charge separation and recombination within an electron donor−acceptor molecule dissolved in nematic LCs. The donor−acceptor molecule consists of a 4-(*N*-pyrrolidinyl)naphthalene-1,8-imide electron donor (PyrNI) covalently attached to a pyromellitimide acceptor (PI).[7] Transient absorption measurements of the electron-transfer dynamics of PyrNI−PI dissolved in the LC *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA) above the nematic−isotropic (N−I) phase transition of the LC show that the solvation dynamics of charge separation and charge recombination in MBBA are highly unconventional and due to the persistence of ordered microdomains in the isotropic phase.[8] Thus, significant anisotropy exists above the clearing temperature of the LC, even though the domain sizes are sufficiently small to essentially eliminate optical scattering.[8] Furthermore, the different temperature dependence of collective

microdomain reorientation vs molecular intradomain reorientation permits a determination of the types of solvent motions that are coupled to the electron-transfer reactions.[9] We show that photoinduced charge separation from the lowest excited singlet state of PyrNI within PyrNI−PI is adiabatic because it is controlled by the collective microdomain reorientation times of MBBA, whereas the thermal ion-pair recombination is nonadiabatic because it is mediated by fast molecular motions within the domains. The results are compared to our studies of the solvation dynamics of photoinduced charge separation and recombination within PyrNI−PI dissolved in the liquid crystal 4′-pentyl-4-cyanobiphenyl (5CB).[5] In 5CB, the opposite result is observed. Charge separation is nonadiabatic, while charge recombination, under the control of the collective solvent response, is adiabatic. The results are interpreted as arising from the different signs of the dielectric anisotropies of the two LCs, where that of MBBA is negative ($\epsilon_\perp \approx 5.4$, $\epsilon_\parallel \approx 4.7$ for a $\Delta\epsilon = -0.7$)[8] and that of 5CB is positive ($\epsilon_\perp \approx 6$, $\epsilon_\parallel \approx 18$ for a $\Delta\epsilon = 12$).[10] In addition, electron-transfer data for PyrNI−PI is presented in 4′-octyl-4-cyanobiphenyl (8CB), which like 5CB is a LC that possesses a positive dielectric anisotropy.

The application of Landau−de Gennes theory to the N−I phase transition within a nematic LC shows that the molecular correlation length $\xi(T)$ of the domains is given by the relationship[8]

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

where ξ_o is the molecular length and T^* is 1−2 K below the N−I phase transition. Equation 1 shows that molecular correlation lengths of approximately 20 exist just above the N−I

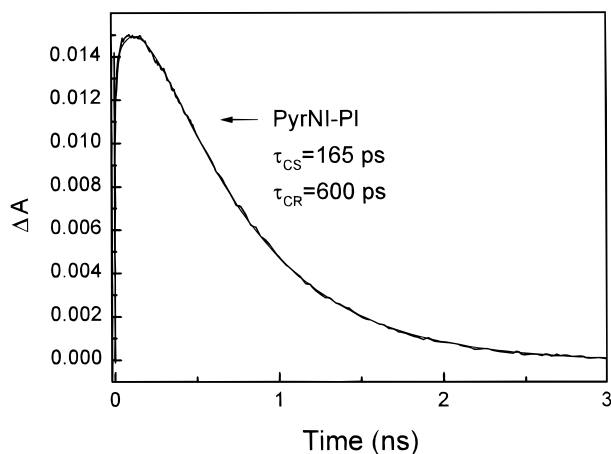[†] Argonne National Laboratory.
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Figure 1. Transient absorption kinetics for PyrNI−PI in MBBA at 328.5 K monitored at 710 nm. The smooth line through the data is the Levenberg−Marquardt least-squares fit.

phase transition and gradually decrease to 3 molecular lengths at approximately 50 K above the phase transition. Recent four-wave mixing experiments have shown that these liquids display reorientational dynamics that consist of long time scale (∼1−200 ns) collective domain reorientation motions in conjunction with faster (<∼200 ps) molecular responses within the domains.[11,12] Furthermore, the fast molecular responses were found to be temperature independent, due to small changes in their local environment as the domains changed in size, whereas the slower, collective reorientational response τ_{or} of the domains was found to have a temperature dependence consistent with Landau−de Gennes theory[12]

$$\tau_{or} = \frac{\exp(E_a/k_B T)}{c(T - T^*)} \qquad (2)$$

where c is a constant and E_a is the activation energy for the shear viscosity of the LC,[12] which has been previously determined to be 29.7 kJ/mol for MBBA[13] and 34.3 kJ/mol for 5CB.[14] The shear viscosity, ν, is known to correlate with the collective reorientation times of the microdomains.[11−14]

Transient absorption kinetics for the reactions: ^{1*}PyrNI−PI → PyrNI$^+$−PI$^-$ → PyrNI−PI in MBBA, shown in Figure 1, were acquired with a femtosecond Ti:sapphire laser system described previously.[15] PyrNI−PI was dissolved in MBBA in a 1 mm path length thermostated cell and excited using a 490 nm, 100 fs, 0.2 μJ laser pulse. A white light continuum was used to monitor the formation of PI$^-$ at 710 nm, where PI$^-$ has a sharp absorption band.[16,17] This permits unambiguous monitoring of PyrNI$^+$−PI$^-$ formation and decay. The unusual solvation characteristics of LCs near the N−I phase transition are evident in that the lifetime of PyrNI$^+$−PI$^-$ is increased by nearly 2 orders of magnitude relative to that in isotropic solvents of similar static dielectric constant.[1,5] Figure 2 shows the results of a temperature dependence study of the charge separation and recombination time constants for PyrNI−PI in MBBA compared to the results observed in 5CB. The phase-transition temperatures for MBBA and 5CB are 320 and 308 K, respectively, and kinetic traces were obtained down to 2 K above the phase-transition temperature for each solvent. This figure clearly shows that the temperature dependencies of charge separation and charge recombination in the two solvents differ greatly. In MBBA, the time constants for charge separation within PyrNI−PI strongly increase as the N−I phase transition is approached from higher temperatures, while the charge recombination time constants

increase only weakly. On the other hand, for 5CB, the time constants for charge separation increase weakly as the phase transition is approached but the time constants for charge recombination increase rapidly.

The data associated with microdomain reorientation in Figure 2 (charge separation in MBBA and charge recombination in 5CB) were fit using eq 2 plus an additive constant τ_o to account for the charge separation (recombination) time above the temperature where microdomains exist. E_a was fixed at the literature values cited above, T^* was fixed at 306.5 K for 5CB and 318.5 K for MBBA, and only c and τ_o were varied. The fits to the data using the literature values of E_a clearly show good correlation with the collective reorientational dynamics of the microdomains. Therefore, the charge separation reaction within PyrNI−PI in MBBA is solvent controlled and adiabatic, whereas the charge recombination reaction within PyrNI−PI in 5CB is also adiabatic. An adiabatic charge separation or recombination reaction implies that the solvent reorientation times are slow relative to the reaction time. In this regime, the reaction times are proportional to the longitudinal dielectric relaxation time (τ_L) of the solvent, which is also proportional to the Debye relaxation time and therefore to the viscosity of the solvent.[1] Since the collective reorientational times are known to correlate with the shear viscosity of the solvent, these collective modes are responsible for the adiabatic behavior.

The charge recombination time of PyrNI−PI in MBBA does not increase dramatically as the phase transition is approached, suggesting that more conventional solvation dynamics are active for this reaction. The semiclassical Marcus equation for electron transfer is given by[18]

$$k = \frac{2\pi V_{DA}^2 \exp(-\Delta G^*/k_B T)}{\hbar (4\pi\lambda k_B T)^{1/2}} \qquad (3)$$

where $\Delta G^* = (\Delta G^\circ + \lambda)^2/4\lambda$. Here, V_{DA} is the electronic coupling matrix element between the donor and the acceptor, ΔG^* is the activation energy for electron transfer, ΔG° is the reaction free energy for charge recombination (ΔG°_{CR}) in the case of MBBA and for charge separation (ΔG°_{CS}) in the case of 5CB, 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 solvent motions that mediate charge separation or recombination are fast relative to the movement of charge. If eq 3 is obeyed, then a plot of $\ln(kT^{1/2})$ vs $(1/T)$ should be a line with slope of $-\Delta G^*/k_B$. Using our data for the temperature dependence of the charge recombination in MBBA, such a plot is illustrated in Figure 3 and yields $\Delta G^* = 0.08$ eV. Also shown is the result for charge separation in 5CB, which gives $\Delta G^* = 0.25$ eV.[5] Since the plots in Figure 3 are linear, it is clear that these reactions are nonadiabatic.

Using these observations, we can draw some conclusions about the different types of molecular motions that stabilize the ion pair in 5CB and MBBA. For clarity, Figure 5 illustrates the rotational motions typically described by the liquid-crystal molecular dynamics community.[19] Rotations about the molecular long axis(or symmetry axis) are referred to as τ_R^{II}, and rotations about the axis perpendicular to the long axis are called $\tau_R^\perp$. It is generally believed that tumbling motions of the type $\tau_R^\perp$ are coupled to the collective microdomain orientational response.[19] Rotations of the type τ_R^{II} correspond to fast, molecular motions that are not hydrodynamic, i.e., they are not influenced by the viscosity of the liquid crystal and therefore do not show a significant temperature dependence as long as the microdomain
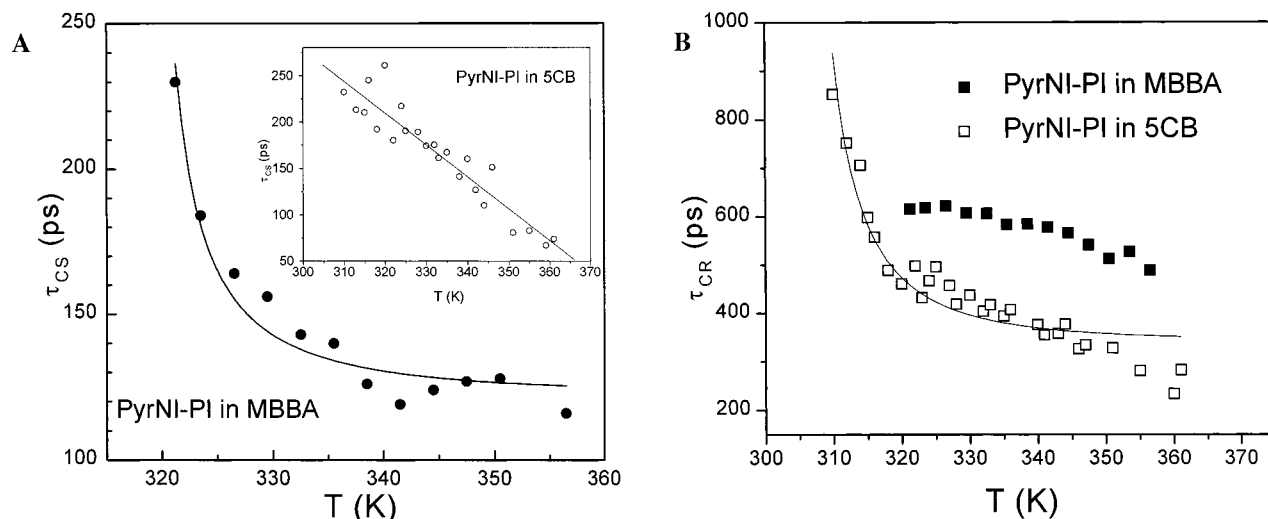
Figure 2. Temperature dependence of the time constants for (a) charge separation (τ_{CS}) and (b) charge recombination (τ_{CR}) for PyrNI−PI in MBBA and 5CB.
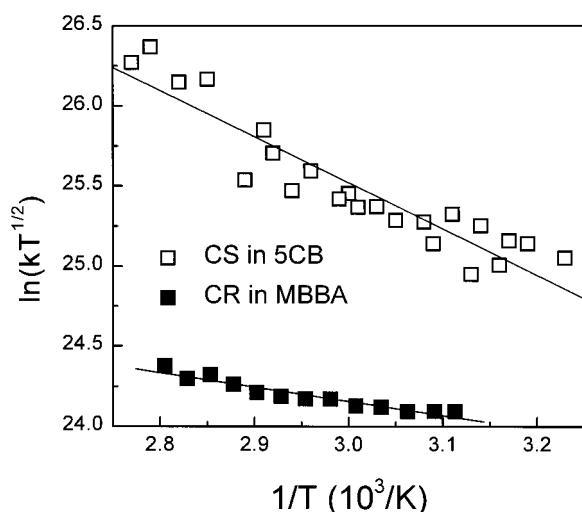

Figure 3. Plot of $\ln(kT^{1/2})$ vs $(1/T)$, where k is the rate constant for charge separation within PyrNI−PI in 5CB and charge recombination in MBBA.
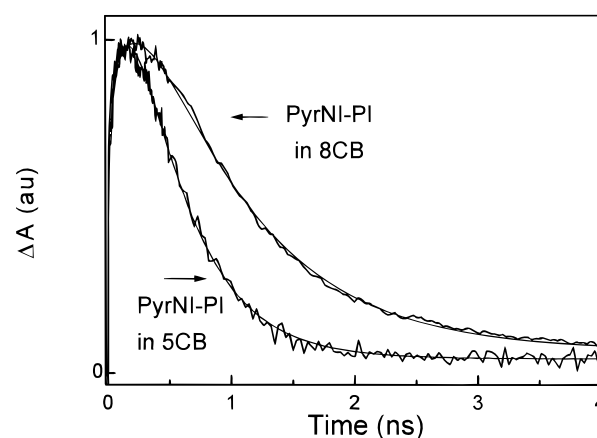

Figure 4. Comparison between the transient absorption kinetics for PyrNI−PI in 5CB at 313 K and 8CB at 319 K monitored at 710 nm. Each temperature is 5 K above the N−I phase-transition temperature. The smooth lines through the data are the Levenberg−Marquardt least-squares fits. The amplitudes of the kinetic traces are normalized for comparison.

size is large enough to shield the molecules from the bulk medium. In other words, the microdomain environment determines the potential-energy surface that establishes τ_R^{II}.[11]

It should be emphasized that this is a simplified version of the molecular dynamics of liquid crystals. For example, translational diffusion can accompany motions of the type τ_R^{II} or $\tau_R^{\perp}$. Furthermore, collective orientational motions related to $\tau_R^{\perp}$ do not consist of one mode but a variety of normal modes with the orientational time of mode q given by[20,21]

$$\tau_q = \frac{\nu\epsilon^2}{L(1 + q^2\epsilon^2)} \tag{4}$$

where q is the wavevector of the mode and L is a force constant. In light of these observations, we can generally say that the electron-transfer reactions which show a steep temperature dependence, i.e., charge separation within PyrNI−PI in MBBA and charge return within PyrNI−PI in 5CB, are controlled by collective, hydrodynamic modes related to $\tau_R^{\perp}$. The reactions that do not show any correlation with temperature and bulk viscosity, i.e., charge return within PyrNI−PI in MBBA and charge separation within PyrNI−PI in 5CB, are related to fast intradomain molecular rotations of the type τ_R^{II}.

The dramatic difference of the ion-pair solvation dynamics in the two liquid crystals may be the result of different orientations of the PyrNI$^+$−PI$^-$ ion pair relative to the micro-domain director. In fact, considering the different signs of the dielectric anisotropy of MBBA and 5CB, it is reasonable and perhaps probable that the lowest ion-pair free energy is achieved with a different orientation of the ion pair relative to the microdomain director. As evidence for a different ion pair/director alignment, we have shown previously that the fit to the data shown in Figure 3 for 5CB permitted the determination of the effective static dielectric constant of 5CB for charge separation within PyrNI−PI.[5] A value of 6 was obtained, which matches the measured value of $\epsilon_{\perp}$.[10] This suggests that rotation of 5CB about its long axis (τ_R^{II}) is the fast solvent response that results in the nonadiabatic charge separation observed within PyrNI−PI. This would be consistent with the rodlike PyNI−PI molecule aligned parallel to the microdomain orientation. In contrast, the adiabatic charge separation observed for PyrNI−PI in MBBA suggests that the tumbling motion ($\tau_R^{\perp}$) correlated with the collective microdomain reorientation of MBBA is the initial solvent response that acts to stabilize the ion pair during its formation. This would be consistent with the rodlike PyNI−
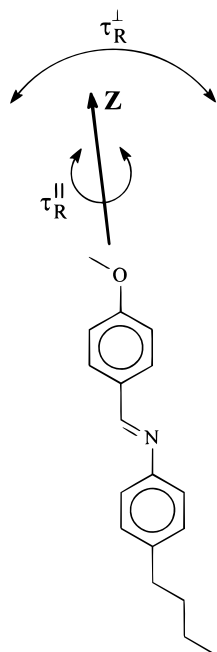
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Figure 5. Molecular motions corresponding to τ_R^{II} and $\tau_R^{\perp}$.

PI molecule aligned roughly perpendicular to the microdomain director.

We also observed the electron-transfer reactions of PyrNI–PI dissolved in 8CB. This LC possesses a positive dielectric anisotropy and a very similar value of $\epsilon_{\perp} \approx 6 \pm 1$ as that of 5CB.[10] The alkylcyanobiphenyls are known to exhibit longer collective reorientational responses as the length of the alkyl chain increases.[22] Therefore, in the framework of our model, the nonadiabatic charge separation rates should be unaffected in 8CB because the value of $\epsilon_{\perp}$ is very similar for both 5CB and 8CB. Moreover, the adiabatic recombination rates in 8CB should be slower than those in 5CB because the collective reorientational responses of 8CB are longer than those of 5CB. This is exactly what is observed, Figure 4, with a charge separation rate similar to that in 5CB and a charge recombination rate that is slower than that in 5CB. The results of this work show that the unusual solvation properties of LCs present novel opportunities to selectively control the rates and mechanisms of charge separation and recombination reactions.

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