Chemically Induced Dynamic Electron Spin Polarization-Detected Energy Transfer. Substrate Size Effects and Solvent Dependence

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Time-resolved electron paramagnetic resonance spectroscopy is used to probe energy transfer from aromatic photoexcited triplet states to azo compounds in liquid solution. The observation of chemically induced dynamic electron spin polarization in the spectra gives precise information regarding the spin physics and mechanism of the energy transfer process. The substrate size is varied by altering the chain length of alkyl chains covalently attached to the azo compounds via ester or amide linkages. The solvent dependence of the energy transfer process is also investigated. The results are discussed in terms of Dexter and Förster mechanisms for energy transfer, the properties of the excited states, and the diffusive properties of the molecules in the solvents of interest. Decomposition rate studies and fluorescence measurements are also reported.

Introduction

Energy transfer is an important topic in photochemistry and photophysics, and many photochemical energy transfer processes lead eventually to free radical reactive intermediates. In a recent study we demonstrated that time-resolved electron paramagnetic resonance (TREPR) spectroscopy can be used to gain insight into the mechanism and kinetics of energy transfer reactions involving photoexcited organic molecules.[1] Chemically induced dynamic electron spin polarization (CIDEP) patterns are often observed in TREPR experiments and are useful because they give, among other information, the spin multiplicity of the excited-state precursor to the radicals. The electron spin state polarization arises because of the creation of non-Boltzmann spin state populations due to singlet−triplet mixing in the radical pairs. Since the intensity of the CIDEP polarization patterns and the rates of the energy transfer processes themselves depend on the relative rate of diffusion of the molecules participating in these reactions, there is often a delicate interplay among ground-state molecular structures, excited-state properties, and solvent properties, all of which can be manifested in the observed TREPR spectra.

Other researchers have reported similar success in following energy transfer processes by examining the TREPR spectra of the reactive intermediates that eventually result. For example, Akiyama et al. showed that electron spin polarization is conserved during energy transfer reactions,[2] and Takemura et al. studied the decomposition of 2,2′-azobisisobutyronitrile (AIBN) by both direct and sensitized photolysis using TREPR spectroscopy.[3] An advantage of the TREPR method is that energy transfer from both the singlet and triplet manifolds can be measured. In this paper, we expand on our earlier study of such phenomena involving aromatic excited states as energy donors and azo compounds as acceptors. We are interested in the effects of solvent and of substrate (azo acceptor) size and diffusion coefficient on the CIDEP-detected energy transfer process.

Scheme 1 shows a simplified Jablonski diagram outlining the concept of CIDEP-detected energy transfer. Species D is a donor with the appropriate excited-state energy levels to undergo efficient energy transfer. The excited singlet state of the donor must have a sufficiently long lifetime for energy transfer to occur. The naphthalenic sensitizers, whose pertinent properties are listed in Table 1, all have S_1 lifetimes between 5 and 100 ns, which, as will be shown experimentally, is long enough for singlet energy transfer to occur. If the sensitizer undergoes intersystem crossing to the excited triplet state or fluoresces to the ground state before coupling to the acceptor molecule can occur, there will be no singlet energy transfer and no subsequent singlet radical pair formation, even though the energy level of the sensitizer may lie above that of the azo compound.

TABLE 1: Sensitizers Used in This Study

sensitizer	E_S (kJ/mol)	τ_S (ns)	Φ_{ISC}	E_T (kJ/mol)	τ_T (μs)
benzophenone	311	0.016	1.0	289	50
naphthalene	385	105	0.80	253	175
1-methylnapthalene	377	70	0.58	254	25
1-chloronaphthalene	375	4.2	0.79	248	280

After singlet energy transfer to the acceptor, the azo molecule has three modes of reaction available. It can fluoresce to the ground state, undergo cleavage to give nitrogen and the radical pair, or undergo intersystem crossing to the triplet state. Linear azo compounds do not have any measurable fluorescence.[4−6] ISC is known to be fairly slow in linear azoalkanes,[7] and this pathway is not expected to be important. Therefore, the major mode of reaction is decomposition to a singlet-born radical pair, which can be detected by TREPR spectroscopy.

In the same manner, the energies of the excited triplet state of the azo compounds can be determined by using CIDEP-detected energy transfer. The excited triplet energy levels of the acceptors range over approximately 90 kJ/mol, with benzophenone having the highest at 289 kJ/mol and pyrene the lowest at 202 kJ/mol. For energy transfer to occur predominantly through the triplet manifold, the donor compound must undergo ISC quickly from the singlet state. Because the lifetimes of the triplet states are 3−6 orders of magnitude longer than those of the excited singlet states, it is reasonable to expect that triplet energy transfer can occur on the microsecond time scale if the

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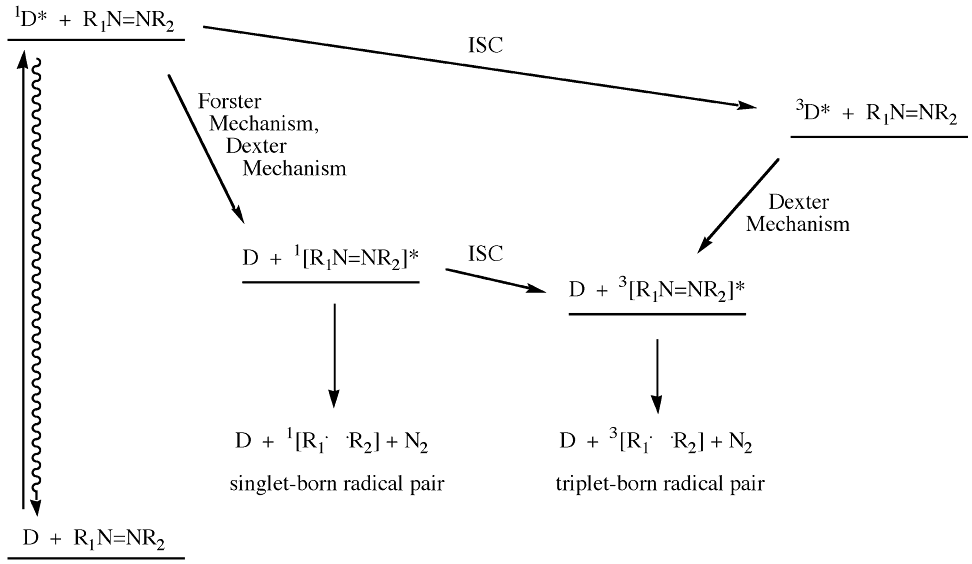
SCHEME 1



donor and acceptor have appropriate energy levels and can diffuse near each other.

As with excited singlet azo compounds, the excited triplet azo compound has several modes of deactivation available, for example, phosphorescence or decomposition to nitrogen and a radical pair. However, phosphorescence of triplet excited linear azo compounds has not been observed,[5,8,9] and therefore, it is expected that only radical pair formation will result from triplet energy transfer from an appropriate triplet sensitizer to the azo compounds.

Triplet energy transfer must occur via the Dexter mechanism,[10] while for singlet energy transfer, the Coulombic or Förster mechanism is usually assumed to be active. This is because the electronic coupling term for the Förster mechanism falls off less quickly with distance than that for the exchange-driven (Dexter) process. However, with long singlet lifetimes and fast solution diffusion rates, singlet energy transfer by the collisional exchange (Dexter) mechanism cannot be excluded. This has been demonstrated experimentally and supported theoretically by Zimmerman and co-workers using freely diffusing samples in solution.[11] Naqvi and Steel calculated the distance of closest approach for a series of azo compounds and aromatic sensitizers to be in the range of 2−9 Å.[12] This is approximately the contact distance between the donor and acceptor, indicating that singlet energy transfer in the compounds studied here is possible through either the Förster or the Dexter mechanism.

Whether it is singlet or triplet energy transfer that occurs will be reflected in the polarization pattern of the CIDEP observed in the TREPR spectrum. Singlet-born radical pairs exhibit multiplet CIDEP in the TREPR spectrum from the radical pair mechanism (RPM)[13] if the sign of the exchange interaction is assumed to be negative for freely rotating molecules in solution. This polarization is predicted to be low-field absorptive/high-field emissive (A/E) for singlet radical pairs. Alternatively, for a triplet polarized radical pair, the RPM polarization will be E/A. Triplet radical pairs can have a second type of polarization from the triplet mechanism, TM. The phase of the TM, either E or A, is a consequence of the symmetry of the donor molecules. For the energy transfer reactions studied here, the TM will be manifested in the TREPR spectrum as completely emissive lines and is strong, dominating the spectrum in many cases. The amount of singlet versus triplet polarization observed in a given radical pair can be determined by computer simulation. Various weightings of the two CIDEP mechanisms (A/E RPM for singlet polarization and E TM for triplet polarization) are added together. The intensities of the two central packets of lines are compared to determine the relative weighting of RPM to TM.

In our earlier study[1] we showed that energy transfer from either the singlet or triplet manifold of a photoexcited donor to an azo acceptor can be controlled through the choice of sensitizer and micellar confinement. The degree of control (from 100% singlet−singlet energy transfer to 100% triplet−triplet energy transfer) can be estimated from the CIDEP polarization pattern as described in that work. A sensitizer with a slow intersystem crossing (ISC) rate, e.g., naphthalene, can lead to energy transfer from the singlet state, whereas benzophenone is a more appropriate choice for triplet sensitization as it has a very fast intersystem crossing rate and long triplet lifetime. This sensitizer dependence, which we have named CIDEP-detected energy transfer, is summarized by the TREPR data shown in Figure 1. Figure 1A shows the TREPR spectrum of radicals from the decomposition of **2** in methanol obtained using naphthalene as the sensitizer, and Figure 1B shows the same radicals from the same azo compound except that benzophenone is the sensitizer.

The spectrum in Figure 1A appears with A/E polarization from the RPM, indicating that the excited azoalkane precursor leading to radical pairs is a singlet state. The observed pure singlet-born RPM polarization can be rationalized by examination of the lifetime of the excited state of naphthalene. Depending on the polarity of the solvent, this lifetime is on the order of 100 ns. From the appearance of the TREPR spectrum, it can be concluded that this is sufficient time for singlet energy transfer to the azo compound to occur before ISC takes place. When the singlet lifetime is very short, as is the case for benzophenone, triplet energy transfer is the preferred route, and this manifests itself in the TREPR spectrum as strong emissive polarization from the TM. To summarize these CIDEP effects, the choice of sensitizer manifests itself in the spectrum of the radicals produced in the eventual photochemistry through the observed polarization pattern (A/E for pure singlet sensitization, A/E superimposed with net E for a competing process (singlet vs triplet), or net E for pure triplet sensitization).

Structural assignment of the spectra in Figure 1 is straightforward. There are six packets of lines due to electron−nuclear

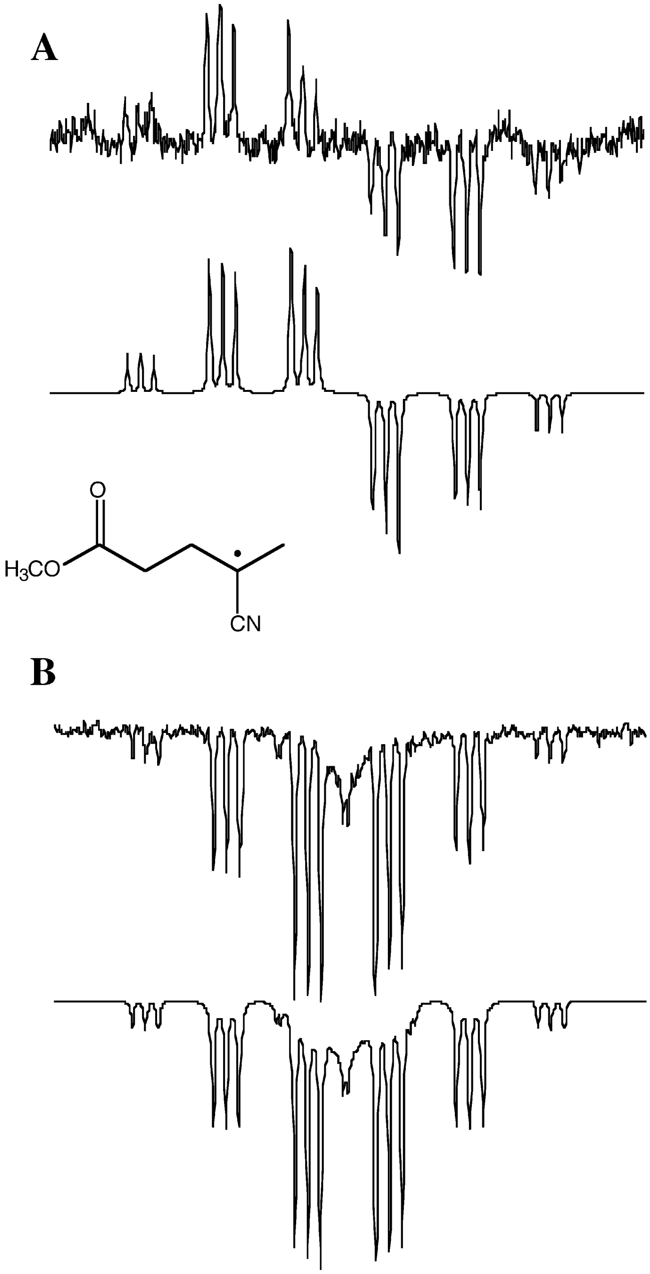
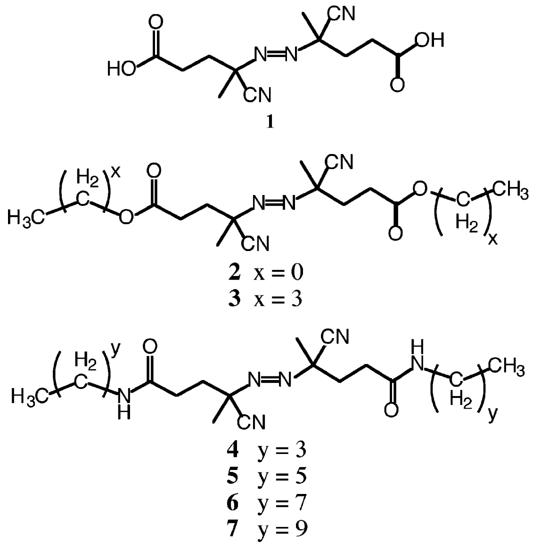


Figure 1. Experimental and simulated TREPR spectra of the photolysis of **2** and (A) benzophenone and (B) naphthalene, both in methanol solution. The hyperfine values used for both simulations are $A_H = 3.3$ G (CN), 20.5 G (CH_3), and 20.9 G (CH_2). In the simulated spectrum for **2** and benzophenone, the polarization is pure triplet mechanism polarization (E), and for **2** and naphthalene, the pure radical pair mechanism (A/E) was used. Line widths were 0.5 G for both simulations. There is a small amount of competition between H atom abstraction from solvent and the energy transfer process. The cluster of signals at the center of (B) (simulated using literature values for *g* factors and hyperfine couplings) are those of the methanoyl radical and the benzophenone ketyl radical.

hyperfine coupling with the three methyl and two methylene protons adjacent to the radical center. The additional 3.3 G splitting of the lines into a 1:1:1 triplet is due to further hyperfine interaction with the γ-nitrogen ($I = 1$) of the nitrile group. Simulations of the spectra using these parameters are also shown in Figure 1. The coupling constants from the methyl (20.5 G) and methylene (20.9 G) protons are almost identical. The slight difference is due to the hindered rotation of the methylene group, but the values are consistent with the literature.[14,15] There is no TREPR evidence of a nitrogen-centered radical being formed on this time scale, as some researchers have suggested.[16]

SCHEME 2



1

2 x = 0
3 x = 3

4 y = 3
5 y = 5
6 y = 7
7 y = 9

The n → π^* absorption of the azo moiety shows a weak band centered around 346 nm and can be monitored optically for the decomposition of the azo compound.[17] The molar absorptivity of this peak is very low, around 20 L/(cm·mol), which is typical for most azo compounds.[18] In all of the work carried out here, the excitation wavelength is 308 nm. In the absence of a sensitizer, this wavelength excites into the $\pi \rightarrow \pi^*$ absorbance of the azo compound, which is not a photochemically reactive state. The amount of singlet versus triplet sensitization from the various donors can be determined from the TREPR spectrum without having to take into account any CIDEP generated from direct excitation of the azo moiety.

The azo acceptor molecules used for this study are shown in Scheme 2. They are derivatives of the common free radical initiator AIBN. A series of symmetric, alkyl-substituted azo compounds was synthesized from the starting material, **1**, which is a commercially available water-soluble initiator from Wako Chemical Co. The UV/vis spectra of the compounds in Scheme 2 do not vary significantly. There is a slight shift of the λ_{max} values, but the difference is less than 7 nm on going from the methyl ester to the hexyl amide.

If azo compound **1** is substituted with alkyl chains of increasing length, steric effects on singlet energy transfer can be studied. Steric effects on energy transfer rates involving azo acceptors have been studied in the gas phase.[19] In that work, an order of magnitude decrease in the rate of singlet energy transfer from azo-*n*-butane to azo-*tert*-butane was observed. In the solution experiments reported here, sterically bulky substituents will play a role in the intrinsic energy transfer rate and also in the rate at which the donor (naphthalene) and the acceptor (modified azo compound) diffuse toward each other. This might be expected to affect which energy transfer mechanism (exchange or Coulombic) is operating,[20] and the CIDEP patterns manifested in the spectra should also change. The structures of the azo compounds have been manipulated in this work by changing the chain length of the alkyl “tail”, as shown in Scheme 2.

Results and Discussion

Azo Acceptor Molecule Structures and General Photochemical Properties. For energy transfer to occur in high yield, two requirements must be met. First, the energy transfer should be exothermic; i.e., the excited state of the donor must lie above that of the acceptor molecule. Second, the rate of energy transfer must be competitive with the rates of all possible additional deactivation pathways for the excited state of the donor. Two different sensitizers were chosen to meet these criteria. The relevant physical parameters of the sensitizers used in this study are shown in Table 1.

It should be noted that direct photolysis of **2** with UV light at 308 nm, in any solvent, does not result in a TREPR signal. If the UV/vis spectrum of compound **2** is compared before and after photolysis, there is no change in the intensity of the peak at 346 nm. This indicates that, in the absence of a sensitizer, there is no loss of the azo moiety and therefore no bond cleavage taking place after photoexcitation of **2** in solution.

It has been reported by Monti and co-workers that, for para-substituted azo benzenes, minimal perturbation of the energetics of azo compounds occurs.[21] They studied azobenzene substituted at the 4 position with diethylamine, methoxide, and nitro groups by energy transfer from aromatic hydrocarbons by flash kinetic spectrophotometry. The lowest excited-state triplet of each of these compounds was found to lie 34 kcal/mol above the ground state of the azo compound. If substitution at the para position on azobenzenes has no effect on the triplet energies, then substitution with alkyl tails five carbons away from the azo moiety in the compounds used for this study should not greatly disrupt the energetic properties of the azo compound excited states. For the above reasons we conclude that the spectroscopic and the energetic properties of the azo moiety are not being strongly perturbed by substitution at the acid terminus of compound **1**.

Engel and co-workers have extensively studied the properties of azo excited states. Because fluorescence of linear azoalkanes does not occur, the singlet energies of these particular azo compounds were not previously known. Azoalkanes (cyclic and linear) do not phosphoresce under normal conditions, so there was little knowledge of their triplet energies and properties. There is only one report in the literature of direct observation of phosphorescence of an azo compound.[22] To observe the phosphorescence, the azo compound was confined to a zeolite host doped with a heavy cation (Tl^+ or Cs^+, for example). By measuring the quantum yield of nitrogen evolution and the rates of fluorescence quenching of azo compounds in the presence of a graded series of sensitizers, Engel estimated the singlet energy levels of several nonfluorescent azoalkanes to an accuracy of 5 kJ/mol.[23,24] In a similar fashion, the triplet energies of azoalkanes (cyclic and linear) were determined by phosphorescence quenching of triplet sensitizers.[7,25]

Engel estimated the energy of the excited singlet state of linear, alkyl azo compounds without the nitrile functionality to be about 310 kJ/mol and that of 2,3-diazobicyclo[2.2.1]hept-2-ene, a rigid bicyclic azo compound, to be 351 kJ/mol. He also showed that, by increasing the rigidity of the molecular framework of the azo compound, the singlet energy level is raised.[26] In the compounds studied here, the quaternary carbon next to the azo functionality will reduce the flexibility of the azo moiety to some extent, and it is expected that the excited singlet energies of these compounds will lie between the energies of the bicyclic and linear azo compounds studied by Engel. The singlet energies of the sensitizers used in this work range from 385 kJ/mol for naphthalene to 311 kJ/mol for benzophenone. See Table 1 for more details.[27]

Diffusion, CIDEP Patterns, and Energy Transfer Processes. The structure of the azo compound has a significant effect on the magnitude of the observed polarization in the radical pair. For example, smaller radicals that diffuse quickly tend to exhibit less polarization due to fewer reencounters with their geminate partner (G pair). The effect of solvent viscosity on the RPM magnitude is reflected in the ratio of the rate of singlet−triplet interconversion and the diffusion coefficient.[13] The intensity of RPM polarization can be expressed as

$$I_{\mathrm{RPM}} = -\mathrm{sgn}(QJ)\,\frac{2|J|\tau_J}{1 + (2J\tau_J)^2}\left(\frac{Qd^2}{D}\right)^{1/2}(\rho_{SS}(0) - \rho_{T0}T_0(0)) \tag{1}$$

where I_{RPM} is the intensity of the RPM polarization, J is the exchange interaction, which is negative for neutral free radicals in liquid solution, τ_J is the correlation time for J, D is the diffusion coefficient, d is the distance of closest approach, and ρ is the matrix element at time zero. The term Q is defined as the rate of singlet−triplet interconversion when J is small and is defined by the following equation:

$$Q = \frac{1}{2}(g_1 - g_2) + \frac{1}{2}\left(\sum_i a_i m_i - \sum_j a_j m_j\right) \tag{2}$$

The first term in eq 1 represents the phase of the polarization of the RPM. For all the systems studied here, J is negative in sign. For singlet-born radical pairs, the overall sign of eq 1 will be negative, corresponding to a spectrum that is low-field absorptive/high-field emissive. The second term in eq 1 is the correlation function for J; the intensity of the polarization depends on the time the radicals spend diffusing between regions of strong vs weak spin exchange. J falls off exponentially with interradical separation. The last term in eq 1 describes the initial excited electron spin state multiplicity, i.e., whether the radical pairs originate from a singlet or triplet precursor.

The Q/D term in eq 1 is the most relevant to this discussion. The the larger Q term, the stronger the polarization will be because it is responsible for singlet−triplet mixing. For example, phosphorus-centered radicals which have hyperfine couplings of greater than 350 G generally show much stronger polarization than carbon-centered radicals (hyperfine couplings between 15 and 25 G) at similar concentrations of precursor and quantum yields of radical production.[28] The influence of the diffusion coefficient on the intensity of the RPM polarization is also important. A large viscosity (smaller D, longer time in regions of strong exchange, higher probability of reencounters) will increase the magnitude of the RPM polarization.

The energy transfer process is also affected by the translational diffusion rate. Slower moving molecules may not undergo sufficient collisions within the excited singlet lifetime to effect energy transfer from that manifold. Taken together, all of the phenomena described above allow us to conclude that the relative rate of diffusion of the donor and acceptor should strongly affect the CIDEP pattern when sensitization is used to create the radical pair.

Changing the Azo Acceptor Structure. TREPR results for compounds **1**, **2**, **4**, **5**, and **7** in methanol are shown in Figure 2. For the unmodified azo compound **1**, energy is transferred predominantly from the singlet state of naphthalene, as shown previously where pure A/E polarization was observed. As the tail length of the chromophore is increased, the amount of net emission in the spectrum also increases, indicating that ISC of the excited naphthalene is beginning to compete with singlet energy transfer to the azo compound. This results in spectra that exhibit polarization due to both the RPM and TM (e.g., Figure 2E). The relative weightings of RPM to TM polarization

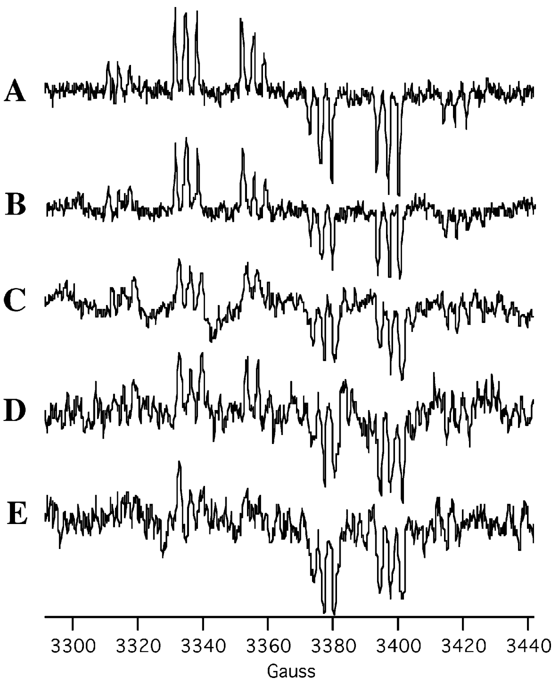


Figure 2. Tail length dependence of the TREPR spectrum in methanol with naphthalene as sensitizer: (A) [**1**] = 0.10 M, [naphthalene] = 0.10 M, 0.9 μs delay time; (B) [**2**] = 0.10 M, [naphthalene] = 0.10 M, 0.6 μs delay time; (C) [**4**] = 0.05 M, [naphthalene] = 0.05 M, 0.6 μs delay time; (D) [**5**] = 0.05 M, [naphthalene] = 0.05 M, 0.2 μs delay time; (E) [**7**] = 0.05 M, [naphthalene] = 0.05 M, 0.2 μs delay time.

TABLE 2: Relative Polarization Intensities

compd	sensitizer	solvent	% RPM	% TM
1	naphthalene	methanol	100	0
2	naphthalene	methanol	90	10
4	naphthalene	methanol	65	35
5	naphthalene	methanol	60	40
7	naphthalene	methanol	55	45
1	naphthalene	benzene	65	35
4	naphthalene	benzene	10	90
5	naphthalene	benzene	10	90
7	naphthalene	benzene	5	95

(obtained by simulation of the TREPR spectrum) are listed in Table 2.

Figure 3 shows the TREPR spectrum of compounds **1**, **4**, **5**, and **7** with naphthalene as the sensitizer in benzene solution. At the shortest tail length, **1**, there is still significant energy transfer from naphthalene in the singlet state. However if the tail length of the compounds is increased from a methyl to a butyl group, the spectrum has much more net emission than the equivalent spectrum in methanol (compare Figure 2C with Figure 3B). Upon increasing the tail length to a decyl chain, the spectrum becomes almost completely emissive. The relative amounts of TM and RPM polarization as determined by spectral simulation for this series are shown in Table 2.

The spectra in Figure 3 show an additional splitting of each of the hyperfine lines because the inequivalence of the methyl and methylene protons is more pronounced. The values of the hyperfine constants used to simulate the experimental spectra are 20.5 G for the methyl group and 21.5 G for the methylene group for Figure 3B–D. This additional splitting is observed only in experiments performed in benzene solutions with azo compounds containing long alkyl tails, probably due to the increased viscosity of benzene (0.65 cP) as compared to methanol (0.51 cP). As the tail length becomes longer, rotation about the C_α–C_β bond to the methylene group is slowed, causing the methylene hyperfine coupling constants to diverge (20.9 G in methanol versus 21.5 G in benzene). The addition of three methylene groups drastically changes the amount of RPM in the spectrum; however, further increases in the tail length do little to alter the dynamics of the azo compound in solution.

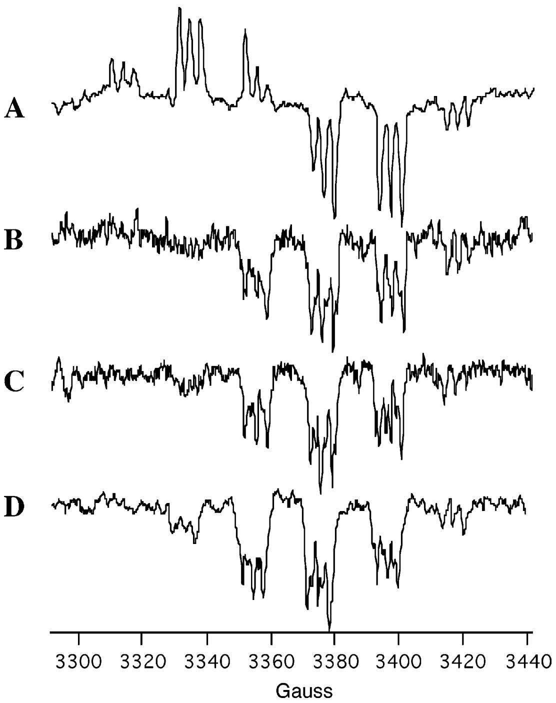


Figure 3. Tail length dependence of the azo compound in benzene as solvent: (A) [**1**] = 0.16 M, [naphthalene] = 0.30 M, 0.4 μs delay time; (B) [**4**] = 0.05 M, [naphthalene] = 0.05 M, 0.4 μs delay time; (C) [**5**] = 0.10 M, [naphthalene] = 0.15 M, 0.6 μs delay time; (D) [**6**] = 0.10 M, [naphthalene] = 0.15 M, 0.6 μs delay time. The sweep width is 150 G for all spectra.

The slight increase in the viscosity of the solution on changing from methanol to benzene cannot satisfactorily explain the observed change in the CIDEP polarization in Figure 3. The change from mostly singlet sensitization to mostly triplet sensitization might be explained by considering energy transfer from the solvent to the azo compound. We consider this possibility because it has been reported that benzene is an effective sensitizer for the cleavage of azo compounds.[12,29] The absorbance of benzene is extremely low at 308 nm, but it cannot be completely neglected because it is present at 40 M concentration. The singlet energy of benzene in dilute alcoholic solution is very high, 459 kJ/mol, but the lifetime is only 29 ns.[30,31] The triplet energy of benzene is 353 kJ/mol, comparable to the energies of the other sensitizers in this study. However, we are forced to rule out this explanation by the result stated above that no TREPR signals are observed in any solvent in the absence of added donors. Another possible explanation becomes apparent by noting that the largest shift in the CIDEP patterns occurs with the acceptor having the longest tail (decyl, **7**). The change is from over 50% singlet polarized RPs in methanol solution to 65% singlet polarized RPs with methyl tails (**2**) in benzene solution. The slower tumbling rate of the longer tailed compounds will lead to slower spin relaxation rates, retaining more of the emissive triplet mechanism spin polarization.

Energy transfer to azo compounds has been shown to proceed predominantly through the collisional, or Dexter, mechanism for both singlet and triplet energy transfer.[19,33] Loper and Lee have measured rate constants for singlet collisional energy transfer from naphthalene to azobutanes.[19,32] They measured a 10-fold decrease of the singlet energy transfer rates for the series

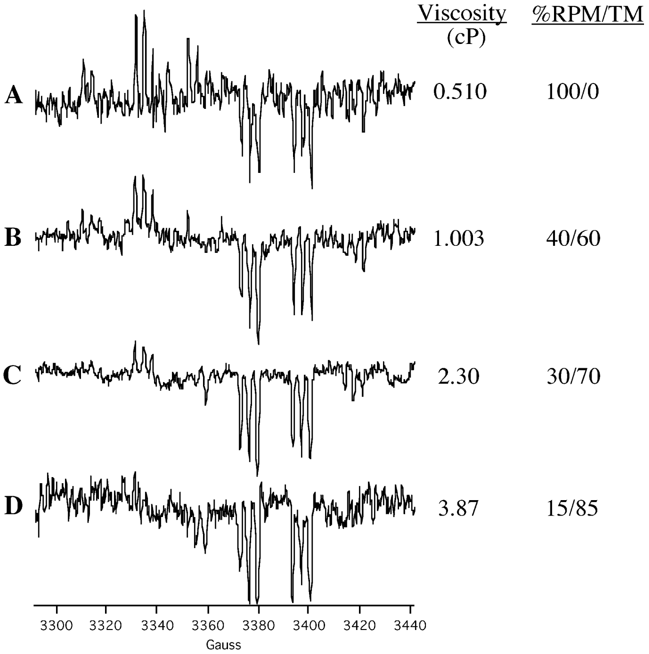


Figure 4. TREPR spectra of the photolysis of **3** (0.05 M) and 1-methylnaphthalene (0.05 M) at a time delay of 0.4 μs in (A) methanol, (B) ethanol, (C) butanol, and (D) hexanol. Values for viscosity come from the CRC and another reference.

n-butane > isobutane > *sec*-butane > *tert*-butane. In the work presented here, a similar steric effect on singlet energy transfer was observed. The general shift from singlet sensitization to triplet sensitization with increasing tail length can be observed in Figures 2 and 3. As the tail length is increased from methyl to decyl, the amount of TM polarization gradually increases. The radical pair spin multiplicity can therefore be manipulated by altering the ability of the donor and acceptor to diffuse together. In our previous study we used micellar confinement of the donor and acceptor to produce similar CIDEP effects.[1]

Solvent Effects. It was shown above how changing the structure of the radical pair precursor changed the relative rate of diffusion of the donor and acceptor in solution, resulting in a change in the polarization of the TREPR spectrum. The same effect can also be observed as the viscosity of the solvent is changed while keeping the structure of the azo compound the same. For these studies, compound **3** was synthesized to increase the solubility of the azo compound in higher molecular weight alkane solvents. A series of alkyl alcohols of different viscosities were chosen as the solvents to keep the polarity and electronic properties of the solvent as close as possible.

If 1-methylnaphthalene is used as the sensitizer, a large change in the relative amount of RPM to TM polarization can be observed with increasing solvent viscosity, as shown in Figure 4. By comparing the intensity of the middle two packets of lines, it can be seen that the polarization is changing from pure RPM for the sample in methanol to TM when the solvent is butanol. The weightings of RPM and TM as determined from spectral simulations are listed on the right-hand side of Figure 4. For singlet energy transfer to be effective, the encounter between the donor and acceptor must occur within the singlet lifetime of the donor molecule. If the encounter does not take place during this time, then the compound can undergo ISC to the excited triplet state, and energy transfer may occur from this state instead. If the viscosity of the solution is increased by changing the solvent from methanol to butanol, the A/E RPM polarization in the TREPR spectrum that corresponds to singlet energy transfer is decreased.

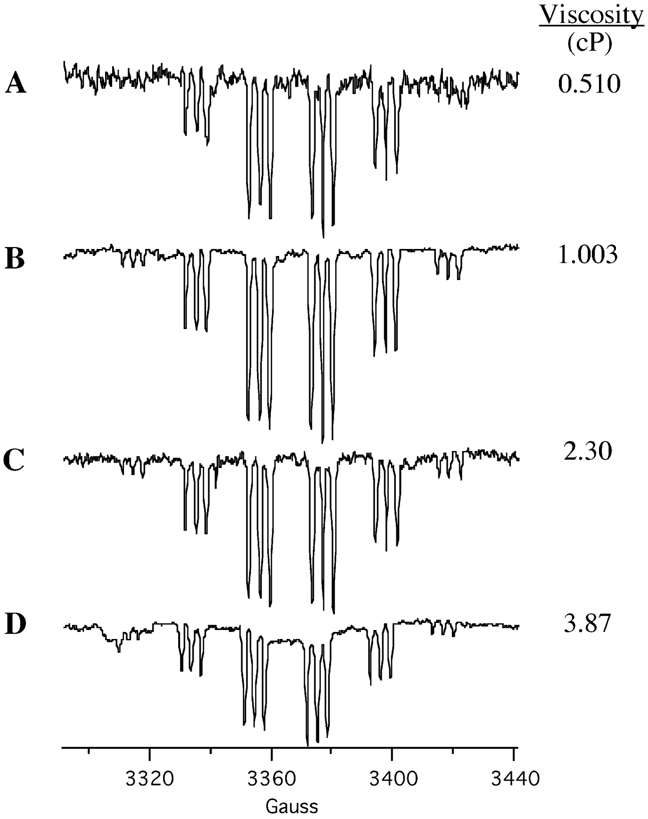


Figure 5. TREPR spectra of the photolysis of **3** (0.05 M) and 1-chloronaphthalene (0.05 M) at a time delay of 0.4 μs in (A) methanol, (B) ethanol, (C) butanol, and (D) hexanol.

The decrease in the amount of A/E RPM polarization relative to that of E from the TM could also be due to the reactivity of the radicals in the solvent cage. Using radical scavengers, Bartlett and Funahashi have found that the escape efficiency of radicals derived thermally from AIBN at 62 °C is ~65% in solution.[33] Further work by Pryor and Smith on the decomposition of peroxide and azo-based initiators has shown that, as the viscosity of the solution is increased, the escape efficiency decreases.[34] There were modest decreases in the escape efficiencies found for azo-based initiators with increases in viscosity. When the radicals are produced via singlet sensitization, chemical reaction is much more likely than if they are produced in the triplet state. This difference in reactivity can lead to an increase in the escape efficiency of triplet radical pairs in solution. The decrease in the amount of A/E RPM polarization is most likely due to a combination of these two effects.

The TREPR spectra of the photolysis of **3** with 1-chloronaphthalene as sensitizer in various alkyl alcohols can be observed in Figure 5. 1-Chloronaphthalene was chosen because of its short singlet lifetime (4.2 ns in methanol), making it a good probe of the role that diffusion plays in singlet versus triplet sensitization. However, by inspection of the CIDEP spectra of the RPs, it can be seen that there is little change of the polarization in the various solvents. The ratio of RPM to TM polarization is around 5/95 for all four samples. We should note that it is possible that the similarity in ratios is due to a relaxation effect or to S−T mixing and therefore may not be as sensitive to RPM processes. Unlike experiments where 1-methylnaphthalene was used as the donor, increasing the viscosity of the solution had no effect on the ratio of singlet to triplet polarization with 1-chloronaphthalene. It is possible that in all solvents the ISC

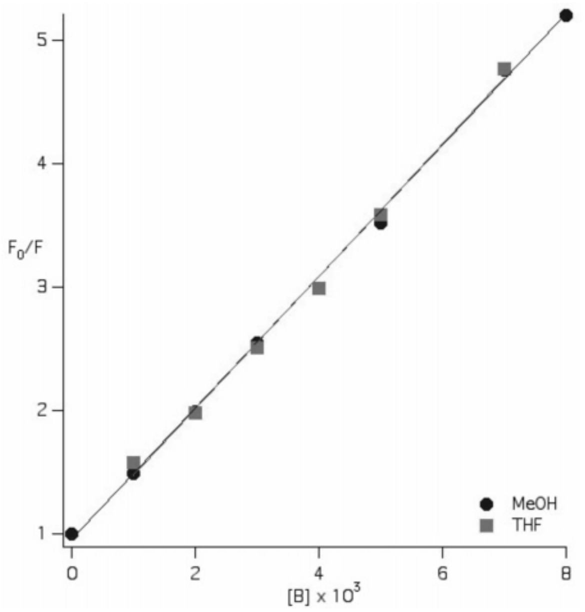


Figure 6. Quantum yield of naphthalene fluorescence versus the concentration of **2** in methanol and THF. The concentration of naphthalene is 1.16×10^{-5} M in THF and 1.18×10^{-5} M in methanol.

rate is very fast and the spin relaxation time in the excited triplet so slow that strong net emission is observed in all cases.

Fluorescence Measurements. The relative diffusion of the donor and acceptor can also be studied using fluorescence measurements. Collisional quenching of fluorescence is described by the Stern−Volmer equation:

$$\frac{F_0}{F} = 1 + k_q\tau_0[\mathrm{Q}] \tag{3}$$

where F_0 and F are the fluorescence intensities in the absence and presence of the quencher (acceptor), respectively, k_q is the bimolecular quenching constant, τ_0 is the fluorescence lifetime of the fluorophore (donor) in the absence of acceptor, and Q is the fluorescence quencher, in this case **1**. If the quenching of the donor is dynamic, i.e., based on diffusion of the donor and acceptor, a plot of F_0/F versus the concentration of the acceptor will give a straight line. If the lifetime of the fluorophore is known, the slope of the line will give the bimolecular quenching constant, k_q.

The bimolecular quenching constant is an excellent indicator of the accessibility of the acceptor moiety to the donor compound. Diffusion-controlled quenching experiments typically return quenching rates of around 1×10^{10} M^{-1} s^{-1}. The more sterically hindered or shielded the acceptor is, the smaller the value of k_q. Wamser et al. have measured the values of k_q for azo-*n*-butane and azo-*tert*-butane and naphthalene in a variety of solvents.[35] They found that the more hindered azo-*tert*-butane has a k_q value that is around 1.5−1.9 times smaller than that of azo-*n*-butane, depending on the solvent. While the ratio of the two k_q values does not depend on the solvent viscosity, the absolute values showed a dramatic dependence on the solvent. Azo-*tert*-butane has a k_q of 8.4×10^9 in pentane. This value decreased to 2.1×10^9 in the more viscous cyclooctane due to slower diffusion in the more viscous solvent.

Figure 6 shows the Stern−Volmer plot for **2** and naphthalene in two different solvents, methanol and THF. Methanol and THF have very similar viscosities ($\eta = 0.51$ and 0.55 cP, respectively) so it is not surprising that the two plots are almost identical. From the slopes, k_q for **2** and naphthalene in both solvents is determined to be 5.1×10^9 M^{-1} s^{-1}. This value agrees well with that determined by Wamser *et al.*[20] and Engel[36] for azo-tert-butane. The value determined in ref 36 for k_q in benzene solution for azo-*tert*-butane ($\eta = 0.60$ cP) was 5.2×10^9 M^{-1} s^{-1}. The viscosity of methanol and THF is only slightly less than that of benzene so it is reasonable that the values are similar.

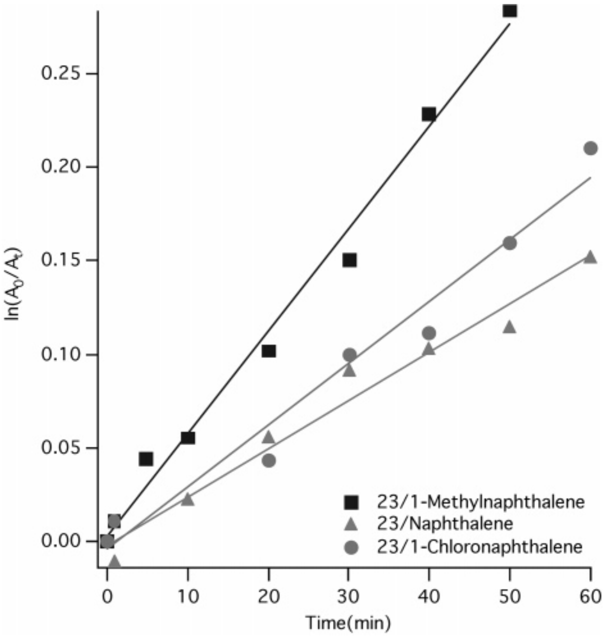


Figure 7. $\ln(A_0/A_t)$ at 346 nm versus time (min) for **2** with various sensitizers: squares, **2** and 1-methylnaphthalene; triangles, **2** and naphthalene; circles, **2** and 1-chloronaphthalene. The concentration of all reagents was 0.05 M in HPLC-grade methanol.

Azo-*tert*-butane and our azo compound **2** have similar steric bulk around the azo chromophore. The similar values of k_q for azo-*tert*-butane and **2** suggest that the presence of the longer tail has little effect on the diffusion of the azo compound and the sensitizer toward each other in solutions of comparable viscosity. The presence of sterically bulky substituents close to the azo moiety appears to be more important to the singlet energy transfer process.

Decomposition Rates. The rate of photochemical decomposition of **1** in the presence of various sensitizers can be measured using UV/vis spectroscopy. This method has been used to study many polymeric free radical initiator systems.[37−39] Because the intensity of the absorption band of the azo moiety at 346 nm is directly proportional to the concentration of the nondecomposed azo compounds, the rate constant for decomposition can be determined with the following equation:[17]

$$\ln\left(\frac{A_0}{A_t}\right) = k_d t \tag{4}$$

where A_0 and A_t represent the absorbance of the azo moiety at times 0 and t, respectively, and k_d is the rate constant of decomposition. Figure 7 shows the graph of $\ln(A_0/A_t)$ for three sensitizers, naphthalene, 1-methylnaphthalene, and 1-chloronaphthalene. Clearly, the rate of decomposition for **1** in the presence of the sensitizers is quite different.

The rate constants for decomposition for the three different sensitizers used to generate Figure 7 are given in Table 3. The experimental values agree well with literature values for the thermal decomposition of AIBN at 55 °C.[17] It is expected that the values for the singlet-sensitized decomposition with naph-

TABLE 3: Rate Constants for Decomposition

sensitizer	slope	$k_d \times 10^{-4}$ (s^{-1})
1-chloronaphthalene	0.00330735	0.55
1-methylnaphthalene	0.00548292	0.91
naphthalene	0.00260529	0.43

thalene and 1-methylnaphthalene will be similar. If the singlet energy transfer is populating the same singlet state of the azo compound (S_1), then the decomposition rates should indeed be the same. As can been seen in Table 3, this is not the case. The value of k_d for the sensitized decomposition with 1-methylnaphthalene is almost twice that of naphthalene.

The differences in the k_d values can be explained by differences in the efficiency of singlet energy transfer from the two donor molecules. In this case, 1-methylnaphthalene has a much higher absorbance at 308 nm than naphthalene. This is a common occurrence in energy transfer reactions. Engel saw a large difference in the quantum yield of nitrogen evolution when 2,3-diazobicyclo[2.2.1]heptene was photolyzed in the presence of different sensitizers.[8] The values ranged from $\Phi = 0.013$ for 2-acetonaphthene to $\Phi = 1.0$ for naphthalene. The ΔE_s for these two sensitizers is only 3 kJ/mol. By fluorescence quenching, Engel also saw that there is a maximum quenching rate, and then as the energies of the donor molecules became greater, the rates of quenching began to fall off. This was assigned to the large difference $E_S(D) \gg E_S(A)$. Energy transfer in this case is favorable, but less efficient.

Because the electronic properties of the singlet and triplet excited states are very different, it is not surprising that the rate constant for decomposition is different when 1-chloronaphthalene is used as the sensitizer. Benzophenone was also investigated in this manner, but its absorbance overlaps strongly with that of the azo moiety, and accurate values for k_d could not be determined.

Conclusions

In this work, it has been shown that both singlet and triplet sensitization of several azo compounds can be carried out in solution and studied by analysis of the CIDEP polarization patterns in the ensuing radical pairs. Appropriate choice of the sensitizer can manipulate the initial spin state of the radical pair, on the basis of donor singlet excited lifetimes and energy levels. Increasing the steric bulk of the acceptor has the effect of slowing diffusion, which makes singlet energy transfer less competitive with fluorescence or ISC depending on the sensitizer chosen.

Experimental Section

Reagents. All reagents and solvents were used as received with the exception of benzophenone and naphthalene, which were recrystallized from methanol. All solvents used in TREPR and fluorescence energy transfer studies were the highest spectroscopic grade available commercially.

TREPR. All spectra were recorded on a JEOL, USA, Inc. RE-1X X-Band (9.5 GHz) CW EPR spectrometer as described previously.[40] The microwave power was 10 mW for all experiments. Laser excitation at 308 nm was produced using a Lambda-Physik LPX 100i excimer laser running at a repetition rate of 60 Hz with laser energies between 140 and 100 mJ, with about one-sixth of the energy hitting the sample. A rectangular cavity was used with a Suprasil flat cell of 0.4 mm optical path length. The samples were bubbled with nitrogen to remove oxygen and continuously flowed to prevent sample depletion and overheating.

Fluorescence Measurements. Emission spectra were obtained with a SPEX Fluorolog 1680 double spectrofluorometer operated in the photon-counting mode with a cooled Hamumatsu R666 photomultiplier tube. Excitation was at 270 nm, and the emission spectra were collected from 290 to 450 nm. For samples in methanol, the concentration of naphthalene was 1.18×10^{-5} M and the concentration of **2** was 1.00×10^{-5} to 8.00×10^{-5} M. For samples in THF, the concentration of naphthalene was 1.16×10^{-5} M and the concentration of **2** was 1.04×10^{-5} to 7.28×10^{-5} M.

Supporting Information Available: Synthesis and characterization details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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