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Energy Transfer Studied Using Spin Polarized Free Radicals. Effect of Substrate Structure and a Comparison Between Micellar Confinement and Free Solution

Vanessa P. McCaffrey and Malcolm D. E. Forbes*

Venable and Kenan Laboratories, CB 3290, Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599, USA

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Abstract—Singlet and triplet energy transfer from a series of sensitizers to three diazo compounds has been investigated in solution and in micelles by time resolved electron paramagnetic resonance (TREPR) of the ensuing free radicals. The singlet lifetime of the sensitizer determines whether the energy transfer occurs from the singlet or the triplet manifold. A radical pair is created after energy transfer by loss of N_2 from the diazo acceptor. The phase of the chemically induced dynamic electron polarization (CIDEP) in the TREPR spectrum describes the multiplicity of the radical pair precursor, and therefore the spectrum carries with it information about the energy transfer mechanism. This principle is established by way of a direct, quantitative relationship between the singlet precursor CIDEP intensity and the singlet lifetime. As the size of the diazo compound is increased, energy transfer from the singlet state is suppressed. Micellar confinement of the radical pair also decreases singlet energy transfer rates significantly. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Non-Boltzmann electron spin state populations, resulting from the phenomenon of chemically induced dynamic electron spin polarization (CIDEP),[1] are often observed in time-resolved electron paramagnetic resonance spectroscopy[2] of free radicals. The spectral patterns observed in CIDEP give important information about the photochemical mechanism leading to and the interactions between the ensuing radical pair. For example, if the sign of the exchange interaction in the radical pair is assumed to be negative, multiplet CIDEP from the radical pair mechanism (RPM)[3] is predicted to be low field emissive/high field absorptive (E/A) for a triplet precursor, and A/E for a singlet precursor. Additional mechanistic information is available if the radical pair shows net polarization from the triplet mechanism (TM),[4,5] which can be E or A depending on the magnetic properties of the parent triplet state. Radical pairs can also exhibit a superposition of the two mechanisms, indicating that radical production and intersystem crossing are competitive processes.

Akiyama, et al. have shown that spin polarization is conserved during energy transfer reactions in fluid solutions, where the donor is photochemically excited and the acceptor is originally in the ground state.[6] Especially pertinent to our work is their study of the CIDEP spectral patterns observed, after radical-producing energy transfer reactions, as a function of the energy gap between the donor and the acceptor.[7] In that work, an acceptor producing singlet radical pairs upon direct photolysis showed pure A/E multiplet polarization from the RPM. Using a series of triplet energy donors with different energies, different amounts of net A polarization were observed superimposed on the A/E pattern. The triplet energy level of the acceptor could be determined from this series of experiments from the overall polarization pattern in the CIDEP spectra. The spectra would show a net contribution from the TM if the triplet energy level of the donor were above that of the acceptor, i.e., when triplet energy transfer was fast, but the pure A/E spectrum would be observed in the donor energy were below that of the acceptor, i.e., when triplet energy transfer was slow.

In this paper we report a similar study of energy transfer using CIDEP observed in the ensuing free radicals. However, the focus of our experiments is different from that in previous work in that we are also interested in the singlet energy transfer process. We have three objectives: (1) to study the effect of substrate structure on the energy transfer rate, (2) to learn about the mechanism of the energy transfer process itself (exchange or Coulombic), and (3) to learn about the effect of micellar confinement on the energy transfer and intersystem crossing processes. To carry out this study we have generated spin polarization in radical pairs produced from the diazo acceptor molecules shown in Scheme 1. Diazo compound **1** is the commercial

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Keywords: azo compounds; electron spin resonance; micellar systems; photochemistry.

* Corresponding author. E-mail: mdef@unc.edu

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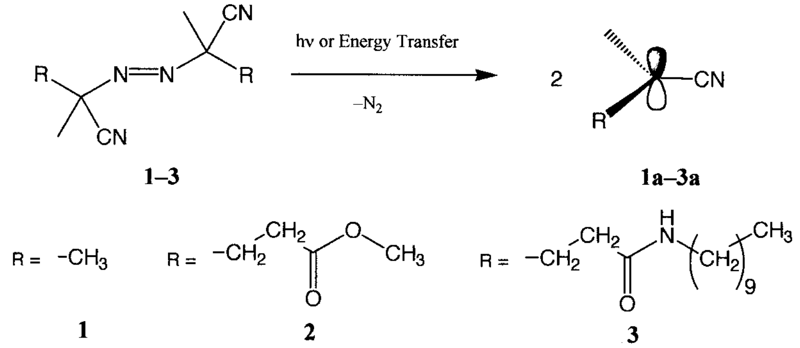


Scheme 1.

polymerization initiator 2,2′-azobisisobutyronitrile (AIBN), and compounds **2** and **3** are an ester and amide, respectively, which are synthesized from the corresponding dicarboxylic acid.

Initially, diazo compounds were of interest to us because they can cleave upon direct photoexcitation to give singlet-born radical pairs. Such pairs, when produced in micelles where diffusion is restricted, are called spin-correlated radical pairs (SCRPs).[8] A detailed analysis of the spectra of singlet-born SCRPs can provide insight into the relative roles of diffusional dynamics, chemical reactivity, and spin wave function evolution in the so-called 'spin chemistry' of radical pairs. In micelles it may also be possible to determine the sign and estimate the magnitude of the exchange interaction, J, between the radical centers of the geminate radical pair, which has been done previously in our laboratory but not with singlet-born SCRPs, which are rare in liquid solution.[9]

A problem in carrying out this experiment is that the absorptivity of diazo compounds is extremely low at 308 nm (ϵ=8–143 L mol^{-1} cm^{-1}). While absorptivity is better at 248 nm (ϵ=9–646 L mol^{-1} cm^{-1}), the quantum yield for production of radical pairs appears to be low at this wavelength of excitation. In order to generate singlet-born radical pairs at a sufficient concentration to be detected by TREPR, the addition of a sensitizer was necessary. The use of different sensitizers led to interesting CIDEP polarization patterns in both free solution and in micelles, from which information can be obtained about the preceding energy transfer processes.

Experimental

Reagents

All reagents were used as obtained commercially unless otherwise noted. 4,4′-Azobis(4-cyanovaleric acid) (V501) and AIBN were donated by Wako Chemicals. All other reagents were obtained from Sigma Aldrich Chemicals.

Characterization methods

All ^{1}H NMR spectra were recorded on a Bruker Model AC-200 (200 MHz). UV/Vis spectra were recorded on a Shimadzu UV-1201 spectrophotometer.

TREPR spectra

All spectra were recorded on a JEOL, USA, Inc. RE-1X X-Band (9.5 GHz) CW EPR spectrometer. The apparatus has been described elsewhere.[10] 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. A rectangular cavity was used with a Suprasil flat cell, 0.4 mm optical path length. The samples were bubbled with N_2 and continuously flowed to prevent sample depletion and overheating.

Methyl ester of V-501 (2)

Prepared by acid catalyzed esterification in neat methanol. 5 grams of solid V501 was dissolved in 150 mL of methanol with a few drops of concentrated HCl. After 7 days, the solvents were removed by vacuum distillation leaving a white solid. ^{1}H NMR: ($CDCl_3$, δ) 1.7 (d, 2H), 2.3–2.6 (m, 4H), 3.7 (s, 3H) UV/vis: λ_{max}: 202 nm (ϵ=692 L mol^{-1} cm^{-1}). The product was used without further purification.

Decyl amide of V-501 (3)

V-501 was dried under vacuum to remove excess water. The acid was then converted to the acid chloride using thionyl chloride. The acid chloride was dissolved in CH_2Cl_2 distilled from calcium hydride and cooled in an ice bath. A total of 4.1 equiv. of decyl amine in 15 mL of dry CH_2Cl_2 were added slowly. After 1.5 h, the reaction was washed with water, 1% HCl to remove excess amine, water and then brine. The solution was dried over $MgSO_4$ and filtered. Solvents were removed by vacuum distillation leaving a yellow solid. The product was purified by recrystallization from warm methanol. ^{1}H NMR: ($CDCl_3$, δ) 0.85 (t, 3H), 1.25 (s, 14H), 1.45 (3, 2H), 1.70 (d, 3H), 2.1–2.55 (m, 4H), 3.2 (q, 2H), 5.9 (d of t, 1H) UV/vis: λ_{max}: 204 nm (ϵ=5034 L mol^{-1} cm^{-1}). MS (FAB) 559.4722 (M+H$^+$)

Preparation of micellar samples

Sodium dodecyl sulfate (SDS) was recrystallized from boiling methanol. Water was house purified and further purified by passage through a Millipore Milli-Q water purification system. The SDS was dissolved in water to make a 0.2 M solution. The solution was then warmed to 60°C and the sensitizer added with vigorous stirring. After the sensitizer dissolved, the solution was cooled to room temperature and the diazo compounds were added. The solution was stirred overnight to ensure complete dissolution. If the diazo compound did not dissolve completely, gentle warming or sonication was used.

Results and Discussion

In the course of this research we have learned that we can control, through choice of sensitizer, the rate of energy transfer from either the singlet or triplet manifold of a photoexcited donor to one of our diazo acceptors, and that the degree of control (from 100% singlet to 100% triplet) can be estimated from the CIDEP polarization pattern as described in the Introduction. A sensitizer with a slow intersystem crossing rate, e.g. 1-methyl 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. After the electronic excitation has been transferred to the diazo compound, bond cleavage with loss of N_2, a process which conserves spin, leads to either singlet- or triplet-born radical pairs. The choice of sensitizer therefore manifests itself in the spectrum of the radicals produced in the eventual photochemistry through the phase of the CIDEP observed (A/E for pure singlet sensitization, A/E superimposed with net E for a competing process, or net E for pure triplet sensitization).

The structure of the diazo compound may have a significant effect on the polarization magnitude in the radical pair and therefore on the overall intensity of the spectrum. For example, small radicals that diffuse quickly tend to exhibit less polarization due to the lower number of re-encounters with its geminate partner. Solvent viscosity and the magnitude of the hyperfine interactions in the radical pair also have such an effect.[11] The polarization phase may also be affected by diffusion rate as slower moving molecules may not undergo sufficient collisions within the excited singlet lifetime to effect energy transfer from that manifold. Below we will show that the rate of diffusion of the acceptor can actually affect the phase of the polarization when sensitization is used to create the radical pair.

Fig. 1 shows spectra obtained at a delay time of 0.6 μs after photoexcitation at 308 nm of diazo compound **2** in the presence of an equal amount of four different sensitizers. The assignment of the spectrum is straightforward[12] with the six packets of lines being due to electron-nuclear hyperfine coupling with the three methyl and two methylene protons adjacent to the radical center. These five coupling constants are identical, and the additional splitting of the lines into small 1:1:1 triplets is due to further hyperfine interaction with the nitrogen (nuclear spin=1) of the cyano group. Photoexcitation of these solutions in the absence of sensitizer

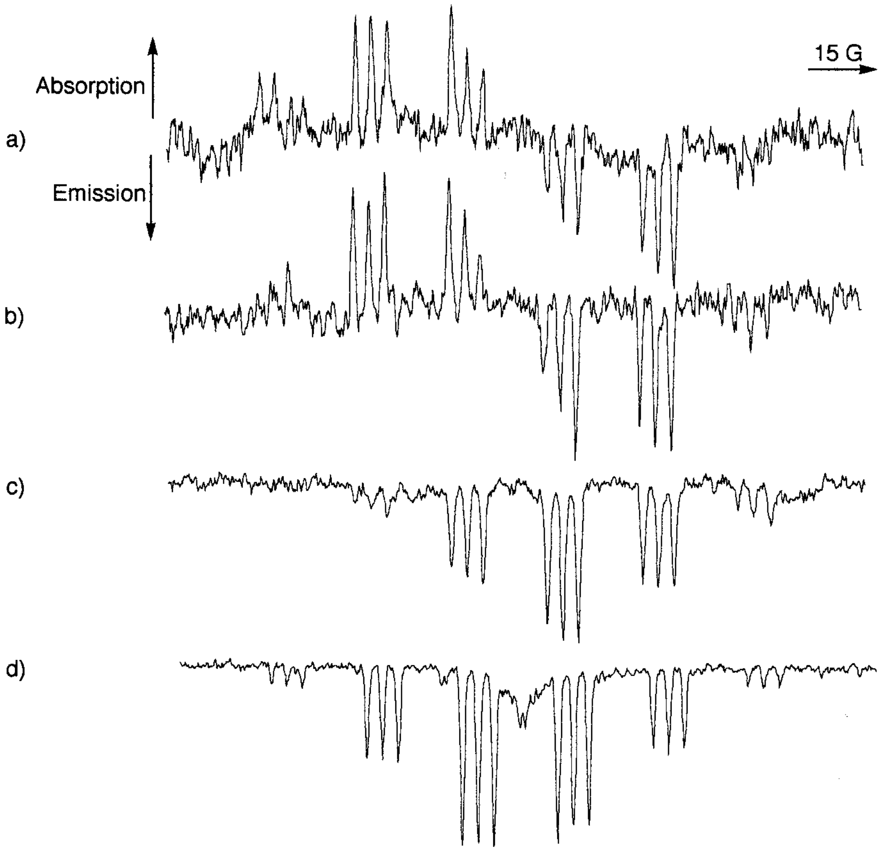


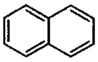
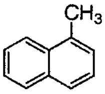
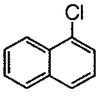
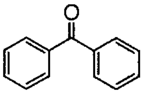
Figure 1. X-band TREPR spectra of solutions of diazo compound **2** in methanol with various sensitizers, collected at 0.6 μs time delay. The following sensitizers were used: (a) naphthalene; (b) 1-methyl naphthalene; (c) 1-chloronaphthalene; (d) benzophenone. All compounds and sensitizer concentrations were 0.1 M.

gave no signal. This is different from the experiments of Akiyama where direct excitation did indeed lead to A/E RPM polarization in the radicals from the singlet excited state of the precursor.

When naphthalene is the sensitizer (Fig. 1a), the spectrum appears with A/E polarization from the RPM, which indicates that the precursor to the radical pairs is a singlet state. The singlet lifetime of naphthalene is quite long; depending somewhat on the solvent used, it is on the order of 100 ns in solution.[13] This is sufficient time to allow for efficient energy transfer to the diazo compound before intersystem crossing to the triplet state occurs. While triplet energy transfer must occur via a collisional exchange process (the so-called Dexter mechanism),[14] singlet energy transfer can occur either by exchange or Coulombic (Förster) mechanisms.[15] The Coulombic process is usually assumed to be more common because the electronic coupling matrix element, which determines the rate in the non-adiabatic limit, falls off less quickly with distance than that for the exchange-driven process. However, with long singlet lifetimes and reasonable diffusion rates, singlet energy transfer by the collisional exchange mechanism cannot be excluded, as the experiments and theory of Zimmerman and coworkers[16] clearly supports for free solution samples; similar support for the collisional mechanism in micelles comes from the work of Wamser et al.[17] The spectrum obtained from photoexcitation of a solution of 1-methylnaphthalene and diazo compound **2** also shows predominantly A/E polarization (Fig. 1b), although by spectral simulation we have determined that there is a very small amount of net E also present (see Table 1). This result is expected since the singlet lifetime of 1-methylnaphthalene is slightly shorter than that of naphthalene, around 70 ns in solution.[18]

When a heavier substituent such as chlorine is substituted on the naphthalene ring (Fig. 1c), the CIDEP pattern changes to predominantly net E plus some A/E. We can tell that this is a superposition by inspection because the outermost packet of lines on the high field side of the spectrum are present but those at low field are not (the multiplet A and net E on the low field side cancel each other's intensity, whereas the net E and multiplet E reinforce each other's intensity on the high field side). The presence of the chlorine on the naphthalene decreases the singlet lifetime of the excited sensitizer to 2.4 ns.[19] In this case energy transfer from both the singlet and the triplet states is occurring, giving RPM (singlet) with TM (triplet) superimposed. We therefore have a most interesting situation where the rates of diffusion, intersystem crossing, and radical production are all approximately on the same time scale. We have observed a similar result when **2** and naphthalene itself are photolyzed in a more viscous solvent, such as benzene. When sensitization is carried out using benzophenone (Fig. 1d) the spectrum shows strong net E, indicating that the radical pairs are formed exclusively from the triplet state of the diazo compound. This result is consistent with the very short singlet lifetime (7–16 ps).[20] There is a small broad emissive signal in the center of Fig. 1d due to H-atom abstraction from methanol by benzophenone triplet, which is a common photochemical reaction for carbonyl triplet states.

Table 1. Correlation of CIDEP pattern with singlet lifetime

Sensitizer	% RPM	τ_S (ns)[a]	ΔE_S (kcal/mol)	ΔE_T (kcal/mol)
	100	105	−15	−2
 	83	70	−13	−2
 	12	2.4	−13	0
 	0	0.016	1	−10

[a] Values taken from Refs. 13, 18–20 respectively.

Table 1 summarizes the observations in Fig. 1 by correlating percent A/E RPM polarization, obtained by spectral simulation, with the excited singlet state lifetime of the sensitizer. This Table and Fig. 1 represents the first observation of radical pairs from the same precursor on the same time scale that are clearly produced with different spin multiplicities through the use of different sensitizers. This result differs from those of Akiyama in that it is the sensitizer changing the multiplicity at all times, i.e. in the absence of sensitizer there is no spectrum. This result was predicted for azo compounds over thirty years ago, even before CIDEP was a fully explained phenomenon, by Engel and Bartlett (they called it a spin correlation effect).[21]

Energy differences between donor and acceptor singlet states and triplet states are also listed in Table 1. The energies used for the diazo compounds are averages of values reported for acyclic azoalkanes.[22] It is noteworthy that in the case of the naphthalene-based sensitizers where some amount of singlet sensitization is seen, the singlet energy level of the diazo acceptor is below that of the donor. In the case of benzophenone, not only is the singlet lifetime very short, but the singlet energy level of the donor lies below that of the diazo acceptor. But because the singlet and triplet energy value used for the acceptor is an average (in fact, several diazo energies from Ref. 22 were well below that of benzophenone), it may not be the case that every diazo compound is indeed in the highest energy excited state. It can be seen that there is a strong correlation of singlet lifetime of the donor with the amount of A/E RPM seen in the spectra, but little correlation is seen with the thermodynamic data. This indicates the observed energy transfer process is diffusion controlled.

Steric effects on energy transfer from naphthalene to a series of increasingly more bulky azo compounds have been studied in the gas phase, with an order of magnitude decrease in rate from azo-*n*-butane to azo-*tert*-butane.[23] In the solution experiments reported here, not only will increased steric bulk play a role in the instrinsic energy transfer rate, but also the rate at which the energy donor (naphthalene) and acceptor (diazo compound) will diffuse towards each other in the first place. This may also have an effect on which energy transfer mechanism (exchange or Coulombic) is operating.[24] We have manipulated the

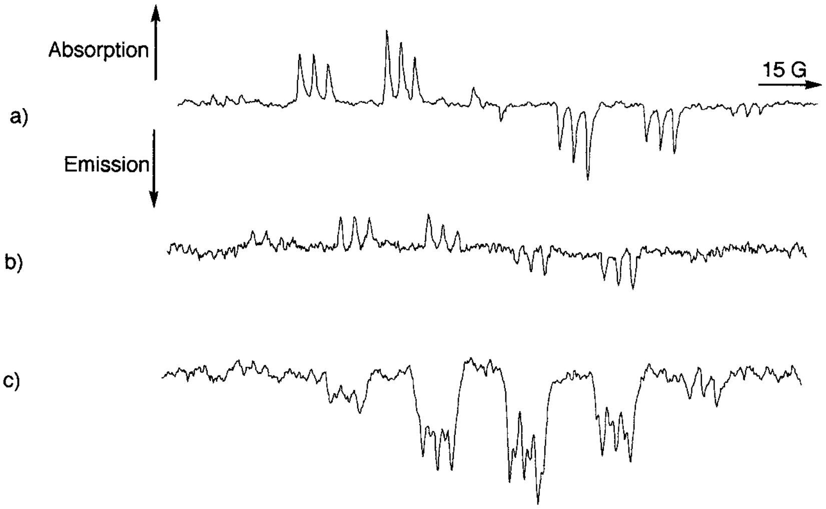


Figure 2. TREPR spectra obtained at a delay time of 0.6 μs in methanol solution using naphthalene as a sensitizer (0.1 M), with 0.1 M concentration of diazo compound: (a) **1** (b) **2** (c) **3**.

structure of our acceptors by changing the chain length of the alkyl portion of the R group in Scheme 1. The results for all three compounds with a constant sensitizer structure are shown in Fig. 2. At the very short extreme of acceptor chain length (diazo compound **1**), energy is transferred predominantly from the singlet state of naphthalene. This is easily concluded from the spectrum in Fig. 2a, where precisely equal amounts of low field A and high field E polarization are observed. It should be noted that radicals formed from **1** have an additional proton hyperfine coupling and so there are 7 packets of triplets instead of 6. The central line in the spectrum has zero intensity, which is in line with the theoretical prediction for a spectrum with an odd number of hyperfine transitions exhibiting pure RPM polarization, in this case from the singlet precursor.

As the tail length of the diazo chromophore is increased, the amount of net E polarization in the spectrum also increases, indicating that intersystem crossing of the excited naphthalene is sometimes occurring before energy transfer is taking place. This can result in spectra that show polarization due to both RPM and TM (e.g., Fig. 2b). In the case of diazo compound **3** (Fig. 2c) energy transfer is occurring predominantly from the triplet state of the naphthalene, as the spectrum shows completely net E polarization. It should be noted that this spectrum also shows an additional splitting because in this particular radical the methyl and methylene protons are no longer equivalent. To summarize Fig. 2, if we make the reasonable assumption that these three compounds all have essentially the same triplet energy, Fig. 2 demonstrates the manipulation of energy transfer rates and radical

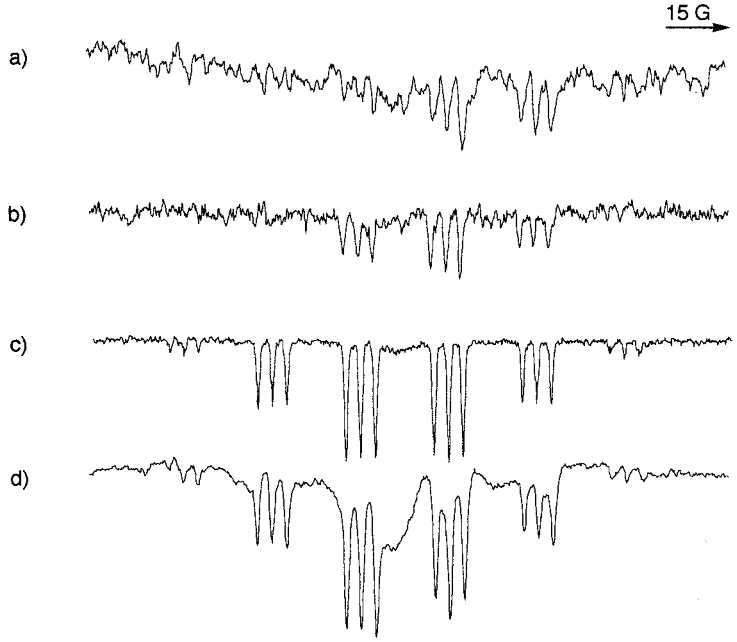


Figure 3. TREPR spectra of **2** in 0.2 M SDS with different sensitizers. Time delay after laser flash is 0.6 μs except (c) 0.8 μs. Sensitizers are: (a) naphthalene (b) 1-methyl naphthalene (c) 1-chloronaphthalene (d) benzophenone.

pair spin multiplicity based entirely on the ability of the precursors, i.e., the energy donor and acceptor, to diffuse together.

We have also investigated the effect of micellar confinement on the energy transfer process. The results of photoexcitation of a 0.02 M solution of compound **2** in a 0.2 M SDS with 0.02 M sensitizer are shown in Fig. 3. For all sensitizers, the observed polarization is net E, although it is clearly stronger polarization for 1-chloronaphthalene and benzophenone than for naphthalene and 1-methylnaphthalene. It should be noted that in the latter two spectra (Figs. 3a and b) there is still a small amount of A/E polarization superimposed on the net E pattern. The results shown in Fig. 3 are unexpected for two reasons. First, in cases of radical formation within the interior of a micelle, spin correlated radical pair polarization is usually observed in the spectrum. This pattern is very different from either the RPM or the TM in that each individual hyperfine line in the spectrum would be split into an emissive and absorptive doublet.[25] This is not seen in any of the spectra in Fig. 3. The dominant polarization is net E, suggesting that sensitization is occurring from the triplet state in all cases, but also that there is no spin correlation (exchange coupling) between the radicals. It is possible that escape of the radicals has taken place and that we are observing only non-interacting monoradicals from the diazo compound. Second, with micellar confinement and the resulting restricted diffusion, it would be expected that collisions would be more probable and therefore the singlet sensitization observed previously for naphthalene and 1-methylnaphthalene would be even more efficient. This does not seem to be the case, in fact quite the opposite.

A possible explanation for the lack of evidence for singlet energy transfer in micelles is that the exchange (Dexter) mechanism, which depends on collisions between energy donor and acceptor, is not operating, and that the rate of singlet energy transfer by the Coulombic (Förster) mechanism is retarded by the micellar environment. The latter could occur if either donor or acceptor has its excited state transition dipole strongly affected by the charges on the micelle head groups or the sodium counter ions. This would require either species to spend most of its time near the edge of the micelle, which is certainly likely based on free volume arguments. Fluorescence, which competes with singlet energy transfer and intersystem crossing, may also be affected by the micellar environment. An alternative explanation is that the more viscous micellar interior prevents sufficient diffusion within the singlet lifetime of the energy donor. This explanation is more palatable because the internal microviscosity of micelles is known to be about an order of magnitude higher than in ordinary liquid hydrocarbon solvents,[26] and there seems to be no logical mechanism to cause a drastic change in the excited state dipoles to support the former explanation. Ndou et al. arrived at a similar conclusion in their studies of energy transfer in cationic micelles.[27]

In benzophenone/SDS aqueous solutions, photoexcitation often results in hydrogen atom abstraction by triplet benzophenone from the alkyl chains of the surfactant.[28] This usually results in a strong SCRP spectrum with individual E/A doublets for each hyperfine line, although if there is significant TM polarization the E/A doublets can be masked. Fig. 3d shows some evidence of this chemistry, with the broad benzophenone ketyl radical signal superimposed in the center, and a few other broad transitions in the perimeter. For all three substituted naphthalene sensitizers (Figs. 3b–d), there is no evidence for this chemistry, which is expected as these compounds are not known to undergo the H-atom abstraction reaction with high quantum yields from either the singlet or triplet excited state.

Summary and Outlook

We have demonstrated that both singlet and triplet sensitization of several diazo compounds can be carried out in solution and studied by analysis of the CIDEP polarization patterns in the ensuing radical pairs. Choice of sensitizer alone can manipulate the initial spin state of the radical pair, based on donor singlet excited lifetimes. Increasing the steric bulk of the acceptor and/or placing donor and acceptor in a micellar environment both have the effect of slowing down diffusion to make either collisional or Coulombic energy transfer less competitive with fluorescence or intersystem crossing. Future work will include the synthesis of donors and acceptors that are linked not just to each other by flexible alkyl chains, but also those that are connected directly to surfactant moieties themselves, to ensure better control of the position of the donor and acceptor in the micellar interior.

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