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Conservation of Triplet Spin Polarization in the Energy Transfer between Triplet Carbonyl Compounds and Aromatic Hydrocarbons in Glassy Matrices. A Time-Resolved Electron Spin Resonance Study

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One important application of electron spin resonance to photochemistry is to obtain information on the excited triplet states as well as the transient species produced in chemical reactions. About a decade ago, we proposed that organic free radicals formed in some triplet-state photochemical reactions are spin polarized, which derived from the initial polarization generated in the triplet-state precursor via the spin-selective intersystem-crossing mechanism.[1] This concept provided the basis for the subsequent establishment of the "triplet mechanism" in the chemically induced dynamic electron polarization (CIDEP) phenomenon.[2-6] The spin-selective intersystem-crossing processes based upon symmetry arguments are well understood,[7] and they have been elegantly demonstrated in a number of chemical systems, including the well-known benzophenone.[8,9] Since triplet photochemistry has continued to generate much interest, the projection that, in some of the triplet carbonyl photochemical reactions, spin selectivity applies to the primary photochemical events of the spin-polarized triplet will have great implications.[10-12] Because of the extremely fast spin lattice relaxation rate of an organic triplet molecule in liquid solution, experiments probing the spin selectivity in chemistry must create a condition in which the chemical rates are favorably competing with the triplet spin lattice relaxation rates.[13] In this communication, we wish to deal with the spin memory conservation in the primary energy transfer processes between a polarized organic triplet and a ground-state organic acceptor. Triplet energy transfer has long been an important topic in photochemistry and photophysics. The possibility of spin polarization conservtion in the energy transfer processes[14] has indeed been demonstrated in at least three systems: phenazine to anthracene,[15,16] quinoxaline to naphthalene,[17] and benzophenone.[18] However, all these three well-known systems involved studies on *single crystals*, and all have relied upon the energy transfer from the host molecules to specifically aligned guest molecules of equal or similar symmetry. Given that the exact mechanism of energy transfer is still not completely understood, the cause of retention of spin polarization during the energy transfer processes must remain uncertain. It may be caused merely by the high degree of order and alignment of the donor and acceptor molecules in the crystal lattice. Since triplet photosensitization is extremely important in organic photochemistry, it is critical to establish the spin polarization conservation in triplet energy transfer among *randomly* oriented donors and acceptors of different symmetry. Furthermore, the effect of interactions between solvent (matrix) molecules and the donor/acceptor pairs on the spin polarization transfer may also be studied in various matrices. The results of our glassy matrices systems of benzophenone and naphthalene and pyruvic acid and naphthalene clearly establish the important aspect of spin specificity in the triplet energy transfer processes by using two different triplet precursors, the benzophenone and the pyruvic acid, which have opposite spin polarization.[19]

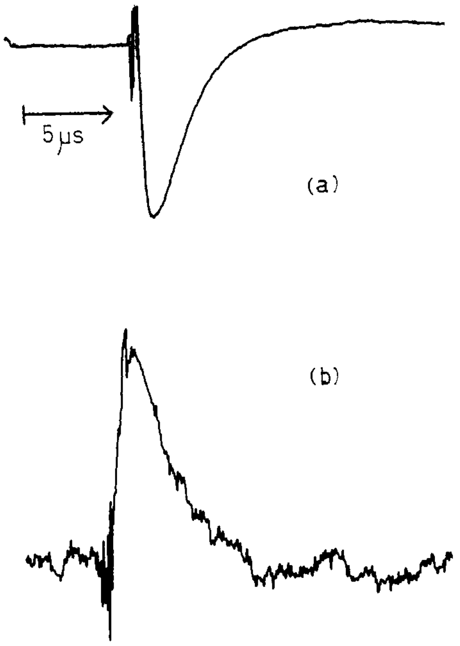

Figure 1. Transient responses of the $\Delta M = 2$ resonance line of the triplet naphthalene in glassy ethanol matrix at 77 K: (a) emission with benzophenone as the triplet energy donor; (b) enhanced absorption with pyruvic acid as the triplet energy donor.

A typical experiment involved a 10^{-1} M ethanol solution containing the carbonyl and the naphthalene compounds. The solution was degassed and then introduced drop by drop into liquid nitrogen to form glassy beads. These transparent beads were irradiated at 77 K within an X-band ESR cavity. For CW observations, a 200-W super-pressure Hg lamp was used. In time-resolved experiments, the glassy beads were irradiated by a Molectron 1.2-MW nitrogen laser. The apparatus of the dc detection and the method of analyzing the transient data have been described.[20,21]

When the glassy beads containing benzophenone and naphthalene were irradiated at 337 nm, the $\Delta M = 2$ resonance line of the naphthalene triplet state was observed at 1460 G, representing a ZFS value, D^*, of 0.1037 cm^{-1}, which is consistent with the literature value.[22] This system is indeed the classic example of triplet energy transfer observed by ESR some 2 decades ago.[23] Since benzophenone intersystem crossing is known to be highly spin specific[8,9] and previous CIDEP experiments in solution[24,25] have concluded that at high field the highest triplet sublevel, P_+, has the highest population (T_z sublevel receives over 95% of the initial polarization[8,9]), it follows that in random glassy solutions it is possible to observe the naphthalene triplet spin polarization, provided the spin polarization of the donor is conserved during

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the excitation transfer and that the rate of the energy transfer is faster than the spin lattice relaxation rate of the benzophenone triplet precursor. The experiment was therefore carried out in the time-resolved mode monitoring at the field of the $\Delta M = 2$ resonance line of the naphthalene triplet. Figure 1a shows the transient emissive polarization observed for the naphthalene triplet in glassy solution. The result suggests that a triplet precursor with a higher P_+ population will conserve this polarization during the energy transfer, thus leading to the acceptor triplet also having a higher P_+ population. It is also clear that the spin polarization conservation in the present example is independent of molecular orientation and molecular symmetry of the donor relative to the acceptor. Indeed, the benzophenone triplet precursor is n,π^* in nature while the naphthalene triplet is π,π^*.

In order to confirm the "sign" aspect of the spin polarization conservation, we have examined the system of pyruvic acid and naphthalene under identical conditions. Pyruvic acid undergoes intersystem crossing at high fields with the P_-, the lowest triplet sublevel at high fields, being the most populated.[19] Thus, the same energy transfer process between the polarized pyruvic acid triplet precursor and naphthalene should lead to the observation of a naphthalene triplet in the enhanced absorption mode. Such an observation is confirmed and shown in Figure 1b.

In the above two systems the triplet excitation transfer involved n,π^* to π,π^*. In order to establish that the excitation transfer between π,π^* and π,π^* triplets also conserves spin polarization, we have examined the systems containing coumarin. In a CW experiment irradiation of a glassy solution containing 10^{-2} M coumarin alone led to the observation of the $\Delta M = 2$ resonance line of the coumarin triplet with $D^* = 0.1249$ cm^{-1}, in good agreement with the literature value.[26] Under time-resolved conditions, the same resonance line exhibited a strong emissive polarization, thus suggesting a highly spin-selective intersystem-crossing process. Optical studies[26] have concluded that the lowest triplet state of the coumarin in polar solvents is the π,π^*, with the triplet energy at 2.56×10^2 kJ mol^{-1}. With naphthalene triplet energy at 2.54×10^2 kJ mol^{-1}, excitation transfer between coumarin and naphthalene is thus probable. When a glassy ethanol solution of coumarin and naphthalene was irradiated in the CW mode, both half-field resonance lines of the coumarin and the naphthalene triplets were simultaneously observed. The time-resolved spectra of both triplets exhibited emissive polarization. Under identical conditions, however, a system containing naphthalene alone did not yield any observation.

It should be noted that all the present experiments were carried out at a magnetic field of about 1500 G. In our early treatment of the random triplet polarization in CIDEP,[33] we have considered that the polarization magnitude may very well be field dependent. Thus, it is not unreasonable to expect that, in the triplet energy transfer processes, both the specificity and the magnitude of the polarization conserved may vary with magnetic field. A critical test for the magnetic field effect would require a variable frequency ESR spectrometer and/or a zero-field spectrometer, which are not presently available in our laboratory.

The current CIDEP results also allow an estimate of the T_1's of the triplets in the glassy solution at 77 K. In all three systems, the naphthalene triplet T_1 was about 2 μs. The T_1 of the coumarin triplet was 3.3 μs. Very few triplet T_1 values are known in literature,[27-29] and almost all of them were measured in single crystals. As a comparison, T_1's of triplet naphthalene in single crystals vary between 6.6×10^{-8} s at room temperature and 3×10^{-4} s at 4.2 K. Recently, the excitation transfer and the relaxation processes of excited triplets in condensed phases have attracted extensive theoretical attention.[30-32] It is hoped that the results reported here will add some insights into the mechanism of spin polarization conservation in excitation transfer, which heretofore has mainly been in the domain of single crystals. The understanding of the mechanism of excitation transfer is a primary step toward the understanding of the overall spin-specific photochemistry.

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Registry No. Benzophenone, 119-61-9; pyruvic acid, 127-17-3; coumarin, 91-64-5; naphthalene, 91-20-3.

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Self-Diffusion of Water at the Protein Surface: A Measurement

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The relative motion of solvent molecules is of considerable interest from both fundamental and applied viewpoints. In the particular case of water at the surface of a large solute particle such as a protein molecule, ideas about the surface mobility of water have spanned the range from rigid or icelike to unperturbed motion as in pure water.[1] In this communication we report an analysis of the frequency dependence of the water proton longitudinal nuclear magnetic relaxation rates measured over a wide frequency range for a protein labeled with a paramagnetic nitroxide probe molecule that provides a measure of the water diffusion coefficient at the protein surface.

The frequency dependence of the nuclear magnetic relaxation rate of water protons in a solution containing a significant concentration of a paramagnetic molecule is dominated by the intermolecular electron–nuclear dipole–dipole interaction. In the case of nitroxide solutes in water this fact has been exploited to measure the correlation times for the solute–solvent interaction.[2-4] While this earlier work may be criticized for the use of a theory less complete than that now available,[5-7] the essential features remain, namely, that the frequency dependence of the proton relaxation of the solvent molecules will provide a measure of the correlation time for the relative translational motion of the water and the nitroxide paramagnetic center. In the present experiment the nitroxide was firmly affixed to the protein by covalent bonds. The reduced mobility of the nitroxide was verified from the EPR spectra. The water proton nuclear magnetic relaxation rate was measured as a function of magnetic field strength corresponding to Larmor frequencies from 0.01 to 30 MHz. The data were analyzed in terms of the translational contribution of the water diffusing in the vicinity of the paramagnetic label on the protein to yield a good estimate for the relative diffusion coefficient for the water and the nitroxide. Since the nitroxide is constrained to translate with a much slower correlation time than that of the

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