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TOWARDS A QUANTITATIVE APPROACH TO THE UTILIZATION OF MAGNETIC EFFECTS AS A MEANS OF ISOTOPIC ENRICHMENT

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Section 2. Accomplished Research (January 1, 1989 - April 1, 1992).

In this section, a brief review is given of the techniques employed for investigation of the magnetic isotope and magnetic field effects at Columbia and of the published research since the last renewal proposal.

A. Experimental Techniques. Selection of Substrates, Environments and Variables for Investigation.

The experimental techniques employed in the accomplished and proposed investigations can be categorized as: (1) spectroscopic and analytical; (2) synthetic; and (3) computational. The interplay of these techniques requires a strongly collaborative and interdisciplinary approach to the accomplished research. The selection of the techniques is determined by the paradigm for magnetic isotope and magnetic field effects discussed in Section 1 and by the goal of characterizing the structure and dynamics of the entities of interest in the paradigm.

The paradigm also provides guidance as to the substrates that should be synthesized to test and to elaborate the working paradigm, as to the environments that should be employed to examine the substrates and as to the variables that will both provide useful information and that will serve as a challenge for a quantitative theory.

B. Time Resolved Techniques Available in the Integrated Spectroscopy Laboratory at Columbia University.

The principal investigator has overseen the construction of an integrated time resolved laser spectroscopy laboratory at Columbia. Six laser systems (two nanosecond YAG lasers, three nanosecond excimer lasers and a picosecond YAG laser) are available to photoexcite ketones with a laser pulse and to trigger the chain of events given by the paradigm of molecular photochemistry. In all cases, the transients are produced by a laser pulse and the detector is triggered to gather the appropriate spectral information after the laser pulse has decayed to a value small enough so as not to interfere with the detection method. For the excimer laser this time is ca 20 nanoseconds and for one of the YAG lasers, this time is ca 10 nanoseconds and for the other YAG this time is ca 30 picosec. The available detection methods are optical density and optical emission, nuclear magnetic resonance, electron paramagnetic resonance and resonance Raman spectroscopy. The time resolution for optical detection and for resonance Raman detection have been in the nanosecond range and has recently (winter 1991) been extended to the picosecond range. The time resolution for electron paramagnetic resonance detection is in the nanosecond range and the time resolution for the nuclear magnetic resonance resonance detection is in the microsecond range.

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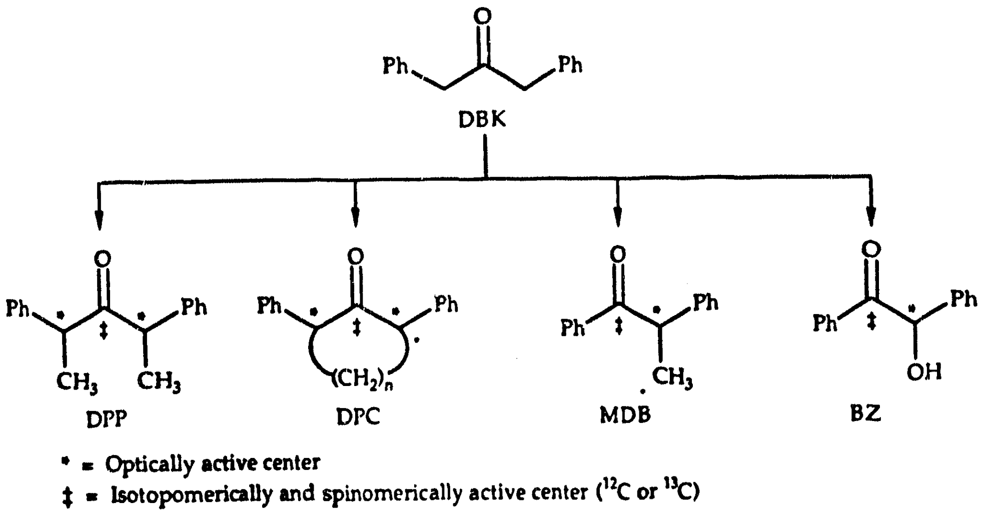
Optical methods are excellent for monitoring the dynamics of transients and allow measurements in the picosecond domain, but are relatively uninformative concerning the structures of transients. The electron paramagnetic resonance method is excellent for structural information on paramagnetic intermediates, but the time resolution is limited to the nanosecond domain. The nuclear magnetic resonance method is outstanding for structural characterization but is limited to microsecond time resolution. Both magnetic resonance methods require the production of polarized species (electron or nuclear polarization) for acceptable signal to noise characteristics in time resolved experiments.

C Synthetic Techniques Available at Columbia. Restricted Reaction Spaces.

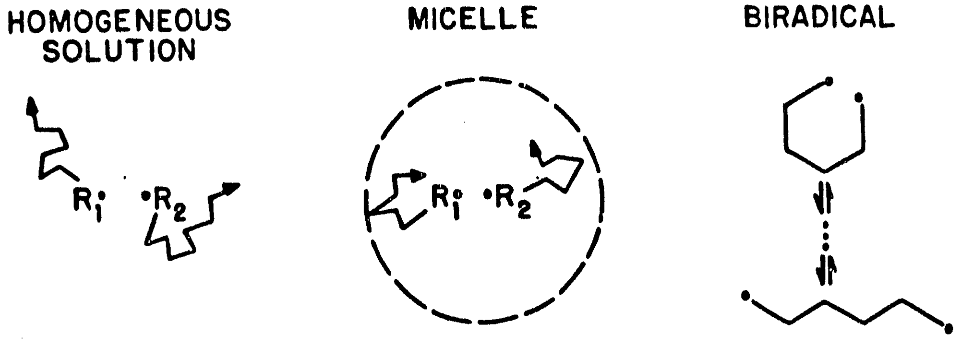
With dibenzyl ketone (DBK) as an exemplar substrate, we have synthesized families of ketones and related structures which allow control and manipulation of the spin dynamics and the chemical dynamics. Scheme 1 shows the structures of some of the families of ketones that have been synthesized and which are representative of the approach. Starting with DBK (which possesses a well defined molecular photochemistry paradigm and



Scheme 1. Outline of the ketone substrates synthesized for investigation. Based on the dibenzyl ketone structure as a starting point, ketones possessing chiral centers adjacent to the carbonyl carbon were synthesized so that the probability, P_r *could be measured directly by measuring stereoisomerization. Also cyclic ketones which produce flexible biradicals of varying lengths were synthesized. Finally, ketones possessing very different chemical dynamics of the radical pair were synthesized.*

generates radical pairs with well defined chemical, spin and molecular dynamics), we have synthesized substrates such as 2,4-diphenyl pentan-3-one (DPP), α,α'-diphenyl cyclododecanone (DPC), α-methyl desoxybenzoin (MDB), and benzoin (BZ). These substrates possess systematic variations in some of the key parameters in the molecular photochemistry of DBK, i.e., the rate constants for α-cleavage and the rate constants for decarbonylation. In addition, each of the ketones can be synthesized as stereoisomers (enantiomers or diastereomers) which provide an access to the probability of geminate combination by measurement of photostereoisomerization. Finally, each can be readily synthesize with a 13-C high content (ca 99%) at the carbonyl carbon atom which provides a unique probe of the role of nuclear spin dynamics on the probability of recombination and on the dynamics of the radical pair.

For each of these substrates, any one of several environments (homogeneous solvents, or restricted reaction spaces such as micelles or zeolites, Scheme 2) can be employed to examine the role of restricted spaces on the probability of geminate combination and the selectivity of isotope separation. In the case of the cyclic ketones, the molecular connectivity provided by a flexible chain of carbon atoms serves as a special sort of restricted space for the radical moieties. The size of the restricted space can be varied systematically for micelles by varying the size of the surfactant making up the micelle and the size of the restricted space can be varied systematically for the biradicals by varying the size of the biradical chain. In the case of zeolites, the restricted space may be varied systematically by varying the size and number of cations occupying the supercages of the internal surface of the zeolite.



Scheme 2. Schematic description of the environment examined for management of the magnetic isotope effect and magnetic field effects on the photochemistry of ketones. The dotted line of the structure in the center symbolizes a micellar or zeolite restricted reaction space.

For a given substrate in a given environment (i.e., a specific acyclic ketone in a micelle or a biradical of given chain length), the probability of recombination or isotope separation selectivity or the dynamics of radical pair (biradical) decay can be measured as a function of variables such as temperature and applied magnetic field strength. The structure of the substrate can then be varied (e.g., compare the structures of DBK, DPP, DPC, MDB, BZ) and the environment can be varied (e.g., size of micelle or for DPC, variation of the chain length) and the external variables of temperature and applied magnetic field can be further investigated. The accumulated information can then be applied to design and test a quantitative theory which attempts to connect experiment and paradigm.

D. Magnetic Field and Magnetic Isotope Effects on the Decay Profiles of Large Flexible Triplet Biradicals.

The DOE supported research on biradicals through 1988 has been summarized in an Accounts of Chemical Research article[1]. The substrates were two families of cyclic ketones and the restricted reaction space was provided by a flexible chain of n carbon atoms. The key experimental parameter was the decay profile of the biradicals which was determined by monitoring the optical density of the biradicals produced by laser flash photolysis of the cyclic ketones. In the absence of an applied external field this decay followed an exponential decay law and allowed the evaluation of a rate constant, k_{bir}, which serves as a parameter to characterize the slow step determining the biradical lifetime. Depending on the substrate either the primary biradical produced (acyl-benzyl) or a secondary radical resulting from decarbonylation (benzyl-benzyl) were monitored and the value of k_{bir} determined.

Measurements were made[1] of the dependence of k_{bir} on n (the number of carbon atoms in the biradical chain), on viscosity (for each value of n), on temperature (for a fixed value of n) and on applied magnetic field (for fixed value of n at variable temperature). The results demonstrated that the lifetime of biradicals are determined by either the chain dynamics or the spin dynamics, depending on the reaction conditions. From the working paradigm, we were able to deduce biradical systems that were dramatically sensitive to the application of a modest external magnetic field. For example, Figure 1 shows that the difference in *the decay profile of an eleven carbon chain biradical can be increased by over an order of magnitude by the application of a magnetic field of only 1000 gauss!* We also showed how different mechanisms for intersystem crossing in the biradicals (spin-orbit coupling, SOC or hyperfine coupling, HFC) generate inherent tendencies for formation of different products. We were able to demonstrate convincingly and unequivocally that extremely small interactions such as very weak electron exchange, SOC in separated radical centers and HFC can produce dramatic changes in the lifetimes and in the product distributions of flexible biradicals.

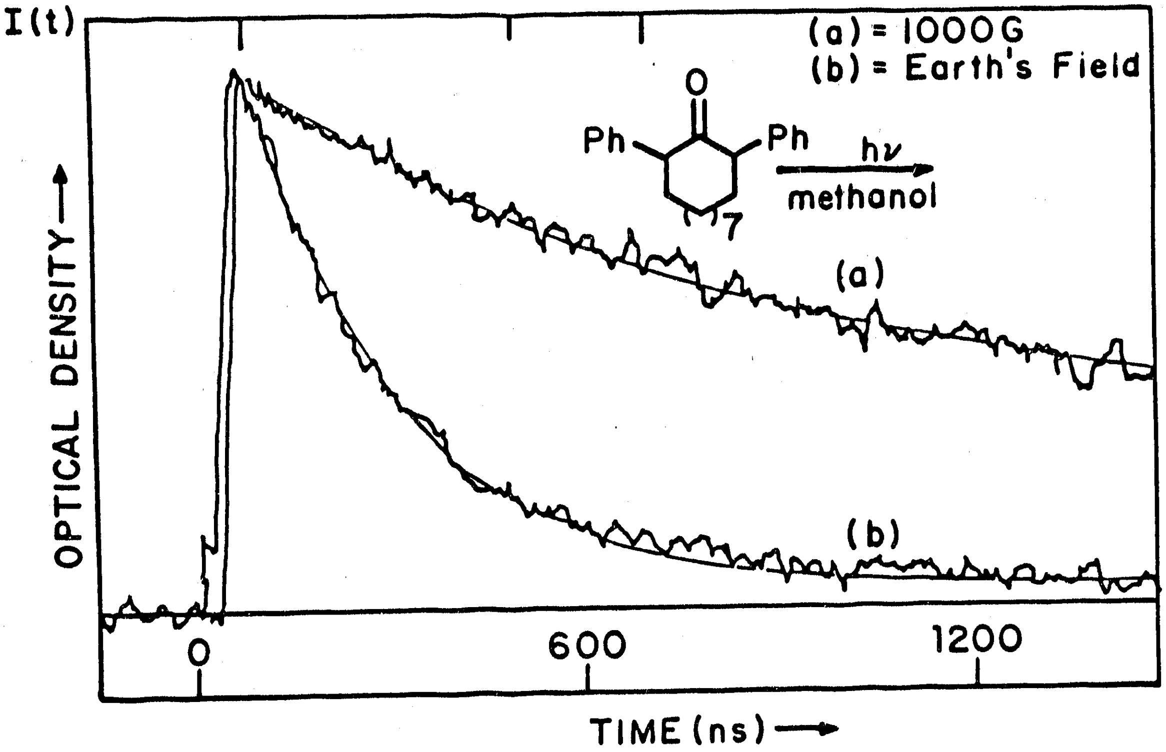


Figure 1. Decay of the optical absorption of the biradical produced from the photolysis of a methanol solution of α,α'-diphenyl cyclododecanone in the absence (bottom trace) and in the presence (top trace) of an applied magnetic field.

During the last period of this DOE grant we investigated the following aspects of triplet biradical systems generated from photolysis of cyclic ketones: (1) the magnetic field effect on the decay profile[2] for hydrocarbon biradicals (derived from cyclanones) of chain lengths varying from 4 to 14; (2) the effect of isotopic substitution, temperature and magnetic field on the magnetic isotope effect[3] of acyl-benzyl biradicals of chain lengths 6 and 12; (3) the activation parameters for triplet biradical decay[4] for hydrocarbon biradicals of chain lengths from 4 to 14; (5) the product distribution, CIDNP and magnetic isotope effect[5] of alkyl cyclododecanones. In addition, we have synthesized and investigated the behavior of 99% 13-C labeled 2-phenylcyclododecanone and of perdeuterated 2-phenylcyclododecanone[6] and the influence of environment (micelles and zeolites) on the product distribution from the photolysis of 2-phenylcycloalkanones[7].

E. Chemically Induced Dynamic Nuclear Polarization of Biradicals.

We investigated the biradical systems generated from photolysis of cyclic ketones by the technique of chemically induced dynamic nuclear polarization (CIDNP). Important information concerning the interplay between chemical dynamics, the spin dynamics and the chain dynamics are potentially available from CIDNP analysis. However, photolysis of the substrates in an NMR spectrometer at 250 MHz did not produce significant CIDNP, thus apparently frustrating the use of this technique to obtain the desired information. We speculated[8,9] that the reason for the failure to observe CIDNP was the absence of an effective pathway to sort nuclear spins in the biradical triplet, i.e., all nuclear spin states were going to the same products and generating the Boltzmann nuclear spin distribution of the products, rather than polarized spin distributions of the products. Reasoning that, according to the paradigm of molecular photochemistry, we should be able to introduce a competing chemically pathway for the nuclear spin states of the triplet that are less effective in promoting intersystem crossing, we were able to find biradical scavengers that induced strong CIDNP.

The success of this concept is shown in Figure 2 for one of the systems investigated[8]. In the absence of radical scavengers, the products of biradicals generated from the photolysis of 2-phenylcyclododecanone does not generate

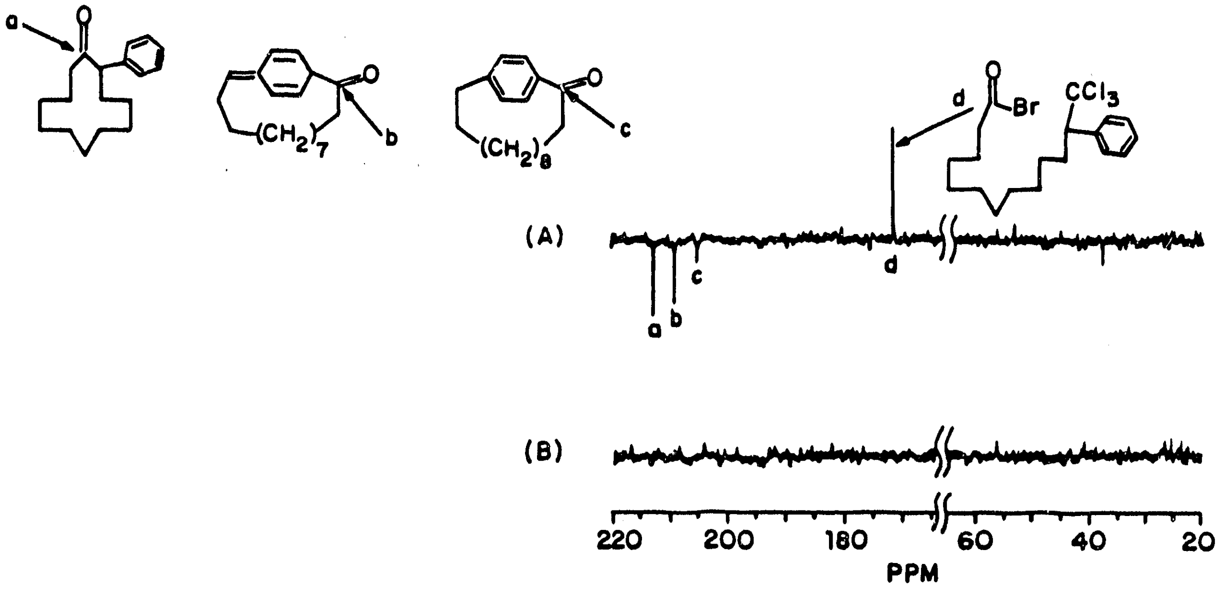


Figure 2. 13-C CIDNP spectrum of 2-phenylcyclododecanone (natural abundance) in acetonitrile in the absence (lower spectrum) and in the presence of $BrCCl_3$. The peak assignments are shown in the structures.

CIDNP at 250MHz. However, addition of $CBrCl_3$ as a radical scavenger induced strong CIDNP, which we associate with the introduction of a pathway for different spin states to proceed to different products, which are then products in non-Boltzmann populations of nuclear spin states. From knowledge of the dependence of the CIDNP intensity on the scavenger concentration and the previously measured lifetimes of the biradical, the rate constant for halogen atom abstraction could be determined.

We also demonstrated by the CIDNP technique the effect of nuclei of interacting nuclei on a given electron spin in a biradical for which a weakly coupled magnetic nucleus can be suppressed by a strongly coupled nucleus[10,11].

F. Computation of Radical Pair Decay in Micellar Systems and Biradical Decay.

Triplet radical pairs in micellar environments and triplet biradicals differ from triplet radical pairs in homogeneous solution in that the "cage" lifetime of geminate pairs in the micellar "supercage" and of the biradical are much longer[12]. The longer geminate correlation of the radical pair and biradical electron spins gives rise to the issue of what mechanisms determine the spin dynamics which determine triplet to singlet intersystem crossing in the micellar radical pair and the biradical. Investigation of the mechanisms of the spin dynamics of micellar radical pairs and the biradicals can be approached by a combination of experimental and computational methods. Some of the questions that are critical for an understanding of magnetic isotope effects and magnetic field effects are:

(1) In micellar systems what are the dominant mechanisms determining the spin dynamics?
(2) How do the contributions of these mechanisms vary with the size of the micelle?
(3) How do the contributions of these mechanisms vary with an applied magnetic field?
(4) How do the contributions of these mechanisms vary with magnetic isotopic substitution?
(5) How do the contributions of these mechanisms vary with substrate structure and varying chemical dynamics?
(6) What are the appropriate models for the molecular dynamics of radical pairs in micelles or the chain dynamics of biradicals?

In order to answer these and related questions, we have collaborated with theoretical groups at the University of Illinois and the Institute for Chemical Physics in Moscow. With the Illinois group we have developed a qualitative model to simulate the time resolved decay of radical pairs in micelles and with the Moscow group we are developing a quantitative model for simulating the probability of radical pair combination in micelles.

G. A Qualitative Model for Micellar Radical Pair Decay.

A theoretical description of the radical pair employing the time-dependent stochastic Liouville equation was found to qualitatively reproduce our experimentally determined magnetic field and magnetic isotope dependence of micellar radical pair decay[13]. An important conclusion of the modeling was that the stochastic variation of exchange interaction, J, with the diffusional motion of the radical pair must be taken into account explicitly in order to obtain qualitative agreement with the experimental data. The experimental data is consistent with the assumption of hyperfine induced intersystem crossing, although the results do not require the absence of other relaxation mechanisms. A similar approach had been employed earlier to qualitatively model the CIDNP behavior of radical pairs in homogeneous solutions and decay of biradicals in homogeneous solutions. Thus, it appears that the time-dependent stochastic Liouville equation, with appropriate modifications for the molecular dynamics in homogeneous solution, for the molecular dynamics in micellar aggregates and for the chain dynamics of biradicals is capable of providing a useful qualitative model for the recombination reactions of geminate radical centers in restricted spaces.

In order to obtain a more quantitative model, it is clear that both more experimental as well as more theoretical investigations are required. On the side of theory a more detailed model of the hyperfine interactions is needed in order to more realistically handle the spin dynamics and a more accurate and physically realistic model for diffusion of the pair in the micelle is needed in order to analyze the contribution of other relaxation mechanisms. Also the spatial dependence of the exchange interaction, the role of diffusional escape of one or both partners from the micelle and the possible role of anisotropic hyperfine interactions need to be addressed. To this extent we propose below (Section 3) an interactive interplay of theory and experiment to probe the questions put forth above as well as others.

H. Magnetic Isotope Effect on Radical Pairs in Micelles.

The photolysis of methyldesoxybenzoin (MDB, Scheme 1), in sodium dodecyl sulfate micellar solutions, produces benzaldehyde and styrene as disproportionation products of the triplet geminate radical pair. We have found[14] that both the benzaldehyde and the recovered methyldeoxybenzoin are enriched in 13-C. These results provide the first direct evidence that both recombination and disproportionation are identically selective to the magnetic isotope effect, an important point anticipated by theory, but previously untested.

An investigation[15] of the photostereoisomerization of the diasteromers of 2,4-diphenylpentane-3-one (DPP, Scheme 1) in micellar solutions has allowed a quantitative analysis of the probabilities of recombination of the micellized primary geminate radical pair toward formation of different combination products. The results show that within the confidence provided by highly accurate data, the primary geminate radical pairs recombine to regenerate the precursor substrate structure or diastereomer with equal probability.

I. Radical Pairs Adsorbed on Zeolites.

Reviews[16, 17, 18] of our research concerning the generation and behavior of radicals adsorbed on the external and on the internal surface of zeolites presented a paradigm that allows for an understanding of how the radical pair diffusional and chemical dynamics can be controlled by the interacting structure of the zeolite and substrate[19]. A spectacular magnetic isotope effect was observed[20] on the product distribution for the photolysis of carbonyl 13-C enriched dibenzyl ketone adsorbed on zeolites. The results were readily accommodated by the paradigm we have developed for the magnetic isotope effect and for the behavior of radical pairs in restricted spaces. In order to obtain further information concerning the sites and dynamics of the ketone substrates adsorbed on zeolites we have investigated[21] the ketone/zeolite complexes by the technique of solid state 29-Si and 13-C NMR spectroscopy and by ESR spectroscopy. The results demonstrated the power and the potential of these spectroscopic methods in providing important information on the substrate, intermediates and products adsorbed in the zeolite systems. We have also shown[22] that the radical pair paradigm can be extended to zeolites, but that in contrast to liquids for which only free radicals and geminate pairs can be differentiated by scavenging, in zeolites the primary and secondary geminate pairs can be separated from each other and from free radicals.

J. Electron Exchange and CIDEP.

The importance of the exchange interaction, J, in determining the selectivity and efficiency of magnetic field and magnetic isotope effects has been emphasized in the introduction (Section 1). For proper understanding of the role of J, we have initiated novel investigations which provide direct experimental information on the magnitude of J and how this magnitude varies with the structure of radical pairs and their environment (or the structure of biradicals and their size. We have published[23] the first comprehensive review of the exchange effect and chemically induced electron polarization (CIDEP).

We have been able to demonstrate experimentally that the charge on a micelle surface can serve to enhance collisions between electron spin polarized radicals produced by photolysis of ketones in micellar systems. Support for these interpretations comes from "scavenging" experiments[24] that employ *electronic spin transfer* to monitor the scavenging. The results of addition of a negatively charged water soluble scavenger nitroxide to the system **1**/sodium dodecyl sulfate (SDS) show (Figure 3) that spin transfer from the polarized radicals to the water bound nitroxide is not observed on the msec time scale. On the other hand, the radical pair generated from the photolysis of **2** completely separates, exits the micelle and the separate radicals transfer their polarization to the water soluble negatively charged nitroxides. However, in Figure 3 we note that for the same system, a cationic nitroxide is able to efficiently "scavenge" the polarization *because the radical pair generated from the photolysis of **1** does not have to leave the micelle to transfer polarization to the micelle bound cationic nitroxides.*

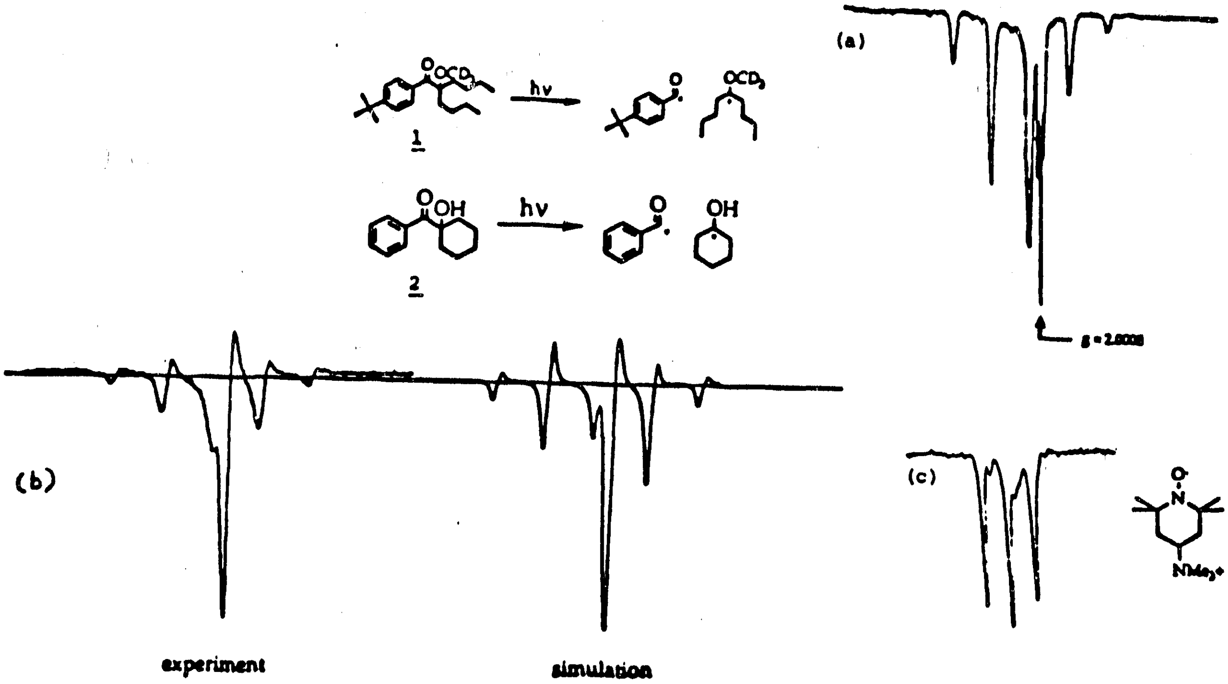


Figure 3. (a) Separated radical pair spectrum produced by photolysis of **1** in homogeneous solution; (b) correlated radical pair spectrum produced by photolysis of **1** in micellar solution, left, and comparison with simulated spectrum, right; (c) polarized nitroxide spectrum (characteristic three line pattern) produced by photolysis of **1** in anionic micelles in the presence of a cationic nitroxide. All spectra taken ca. 500 ns after excitation.

We used the spin polarization transfer to demonstrate that the spin polarization, efficiently generated as the result of triplet sublevel selective intersystem crossing, can be selectively transferred *intramolecularly* to a nitroxide[24]. The latter polarized nitroxide, in turn, can transfer polarization *intermolecularly* to another nitroxide. This "tandem"electron spin polarization ($\neq$) transfer ($S_1 \longrightarrow {}^{\neq}T_1 \longrightarrow R_2$14-NO$^{\neq} \longrightarrow R_2$15-NO$^{\neq}$) is depicted in Figure 4, which shows the time resolved ESR spectra of *tert*-amyl alcohol solutions containing the benzophenone/14-N nitroxide **3** and the 15-N labeled nitroxide **4**. Photolysis of **3** results in electronic spin polarization on the carbonyl groups of the benzophenone moiety of **3** as the result of

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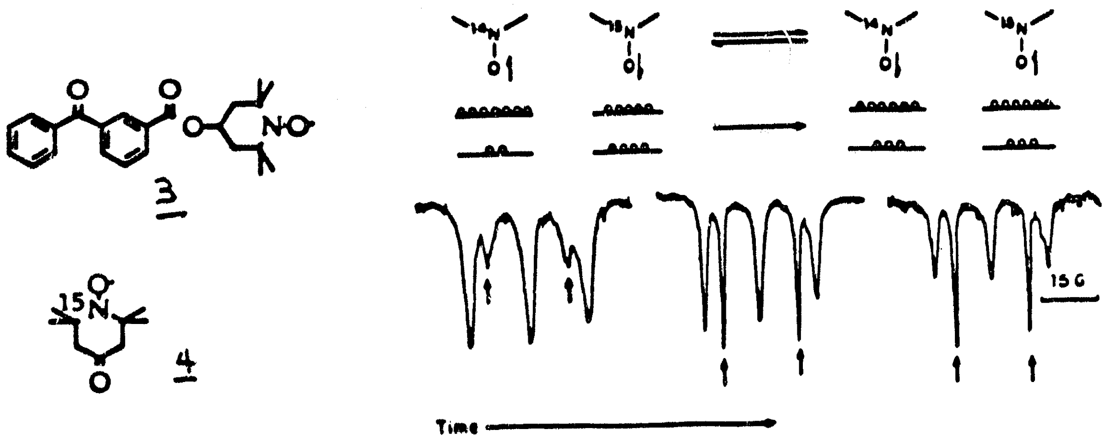

Figure 4. Time resolved ESR spectrum of the system 3 plus 4. The earliest time spectra were taken ca. 500 ns after the laser excitation pulse, and the last spectrum was taken ca. 2000 ns after the laser excitation. Arrows indicate transitions in the ^{15}N labeled nitroxide.

K. Photoelectron Transfer from Metal Complexes Adsorbed on Anionic Interfaces.

Dynamics of the electron transfer quenching of photoexcited $Ru(phen)_3^{2+}$ by methyl viologen in solutions containing various anionic micelles and anionic starburst dendrimers were investigated by the single photon counting technique by monitoring the luminescence decay of the excited complex[25]. Analysis of the kinetics of luminescence quenching revealed that the quenching process in higher generation (>3.5 G and higher) starburst dendrimer solutions obey a general kinetic model previously employed for micellar solutions. In these cases the intramicellar or intrastarburst quenching rate constants (k_q) were found to be unimolecular and decrease with increasing size of the host. In the case of lower generation starburst dendrimers (2.5 G and lower) as with smaller micelles (C-7 and C-8 alkyl sodium sulfates) the quenching reaction was found to be bimolecular in nature. This bimolecular quenching is attributed to the rapid exit of the probe from these macromolecules into the aqueous phase during its life time. Quenching studies using an anionic quencher such as $K_4[Fe(CN)_6]$ substantiates this conclusion. Thus, in spite of the obvious structural differences between micellar aggregates and dendrimer molecules, some striking similarities exist in the ability of both types of restricted spaces to mediate and control electron transfer process conducted on their surfaces.

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