An Electron Spin Polarization Study of the Interaction of Photoexcited Triplet Molecules with Mono- and Polynitroxyl Stable Free Radicals

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Time-resolved electron spin resonance (TR ESR) has been used to investigate the chemically induced dynamic electron polarization (CIDEP) generated by the interaction of stable free radicals with the triplet states of benzophenone, benzil, and 2-acetylnaphthalene. The stable radicals were mono-, di-, tri-, and tetranitroxyl free radicals possessing the 2,2,6,6-tetramethylpiperidine-*N*-oxyl moiety. All of the stable radical systems investigated were found to be emissively polarized by interaction with the triplet states, and the phase of polarization was independent of the sign of zero-field splitting (D) of the interacting triplet molecule. Possible and likely mechanisms of polarization transfer (creation) resulting from the interaction of photoexcited triplet molecules with nitroxyls in the strong electron exchange are discussed. The emissive CIDEP of nitroxyls observed in the interactions with triplet benzil, which has $D > 0$, provides strong support for the operation of the radical–triplet pair mechanism. Within the time scale of TR ESR experiments ($\sim 10^{-7}$–10^{-6} s) no significant variation in the shape of the CIDEP spectra of the nitroxyls was observed, either in viscous media or in micelles. It is concluded that intramolecular spin exchange (or conformational change) of polynitroxyls occurs much faster than the time resolution of the experiment.

Introduction

During the past decade, time-resolved electron spin resonance (TR ESR) studies of phenomena involving electron spin polarization (commonly grouped together under the term of chemically induced dynamic electron polarization (CIDEP), even for systems not involving chemical reactions), particularly in the area of electron polarization transfer, have produced valuable data concerning dynamics of elementary steps of photochemical reactions involving free radicals.[1-6] Electron spin polarization transfer studies can also reveal information relevant to bimolecular collisions in liquids[1,7] and can provide information concerning the details of the mechanism involved in polarization creation.[1-7]

The two most frequently invoked mechanisms for generating CIDEP are the radical pair mechanism (RPM) and triplet mechanism (TM).[1-7] In the RPM, the observed CIDEP occurs *after* the radicals are produced and the polarization is generated by radical pair interactions modulated by exchange interactions and the hyperfine selective reactivity of the pair. Pure RPM is characterized by CIDEP spectra which appear partially in emission and partially in absorption (E/A or A/E, so-called multiplet spectra). In the TM, the observed CIDEP occurs *before* the radicals are produced and the polarization is generated in two steps. First, the triplet sublevels are polarized by (spin–orbit induced) sublevel selective $S_1 \rightarrow T_1$ intersystem crossing; then the polarization generated in the triplet manifold is transferred by rapid reaction to form the radicals. Pure TM is characterized by CIDEP spectra which appear as pure emission or pure absorption (E or A, so-called net spectra). The selectivity of the triplet sublevel population is given by the sign of the zero-field splitting, D; i.e., the sign of the zero-field splitting determines whether the CIDEP spectrum is in emission or absorption. In many experimental examples,[1-7a] the observed CIDEP spectra are superimpositions of the RPM and TM generated polarizations. In addition to these two conventional mechanisms, novel mechanisms of polarization creation have been proposed recently.[8-10] In particular, a mechanism involving the interaction of *nonpolarized triplets and doublets*, which involves the zero-field splitting of the triplet and hyperfine interaction-mediated mixing of quartet and doublet states,[8-10] has been proposed and has been termed the radical–triplet pair mechanism (RTPM). Pure RTPM is characterized by pure emissive or pure absorptive polarization (E or A), but in contrast to the situation for TM, the sign of the polarization is independent of the selectivity of the triplet sublevel population; i.e., the sign of the polarization is independent of the sign of the zero-field splitting parameter, D.

The CIDEP generated by TM may be transferred to radicals, and a number of examples of such transfer to stable nitroxyl radicals have been proposed.[1,7,11] In general, the sign of the observed CIDEP has been total emission, and this result is consistent with the sign of the zero-field splitting (ZFS) for many of the triplets investigated. However, some examples have been reported for which the sign of the CIDEP does not correlate with the sign of the zero-field splitting.[1,8,9] These systems have been explained in terms of the RTPM. As a result of triplet-state quenching by radicals of the 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) family, emissively (E) polarized as well as hyperfine-dependent (E*/A) polarized TR ESR signals have been observed;[1,7,9,11] the specific spectrum pattern basically depends upon the nature of a triplet state and its rotational diffusion, among other factors.[9]

The present investigation involves a TR ESR study of electron spin polarization transfer from photoexcited triplet states to stable mono-, di-, tri-, and tetranitroxyl radicals. From an investigation of their steady-state spectra, the polynitroxyl radicals possess conformations which, at the spectroscopic level, correspond to strong intramolecular spin exchange and are therefore characterized as stable electronic spin triplet (five-line spectrum), quartet (seven-line spectrum), and quintet spin systems (nine-line spectrum). (The number of lines results from electron spin coupling with ^{14}N, a spin = 1 nucleus.) As a result, they serve as interesting model systems for an investigation of the "selection rules" for polarization transfer to acceptors of different multiplicities, and the results of such investigations can be compared to those for the well-studied electronic spin doublet systems.

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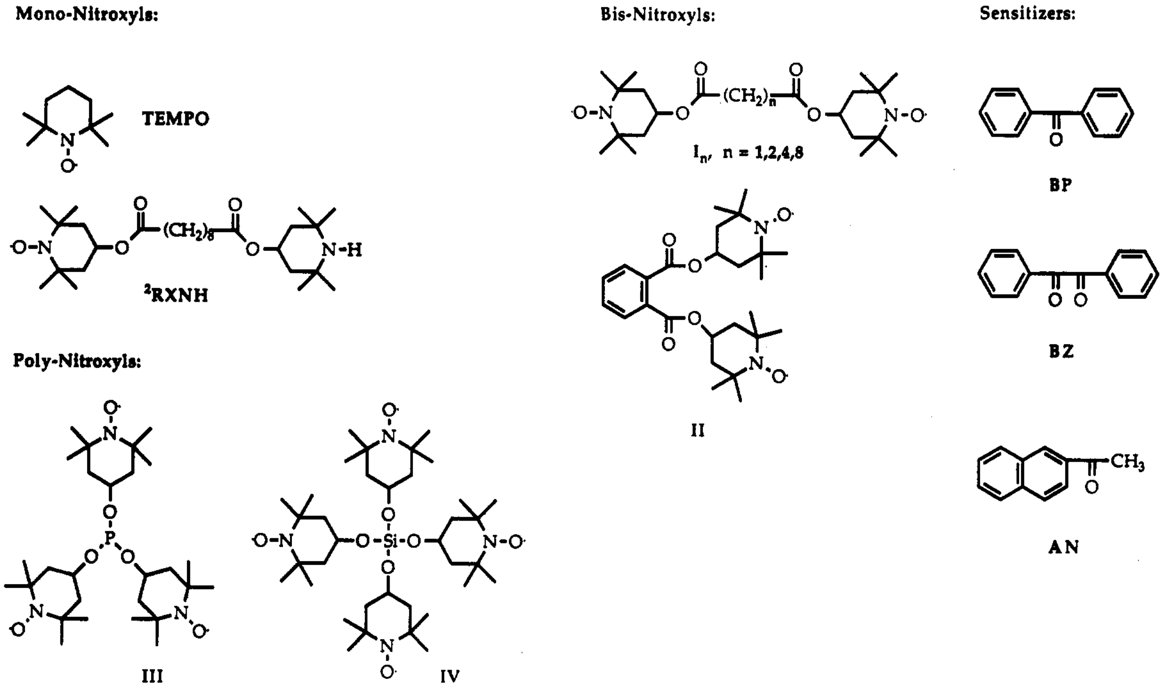


Figure 1. Structure and designations of mono- and polynitroxyls and ketones employed in this investigation.

A particularly intriguing issue of this investigation was the possibility that spin polarization transfer might occur on a "weakly exchange coupled doublet" electronic state of one of the polynitroxyls and that the "weakly exchanged coupled doublet" spectrum (triplet) might then evolve into a strongly exchanged multiplet (quintet, septet, or nonet). Of further interest are those cases where the dinitroxyl radicals possess conformations which slowly interconvert on the ESR time scale and which show simultaneous doublet and triplet conformations in solution.[12] Such systems are candidates for monitoring, by TR ESR, the intramolecular conversion of a doublet system to one of higher multiplicity via the time evolution of the spin polarization. As another point of interest, the dinitroxyl radicals serve as stable models of transient polarized diradicals.[13]

Experimental Section

1. Instrumentation and Procedures. The TR ESR apparatus is of the continuous wave type and has been described previously.[7a] The instrument consists of a Bruker ER 100 D spectrometer, a PAR Model 4402 digital boxcar integrator, a Quanta Ray DCR 2A Nd:YAG laser (8 ns fwhm), and a Bruker broad-band preamplifier with response time of 60 ns. The ESR signals were detected at variable delay times after the laser pulse using integration times of 50–500 ns. The instrument response time was estimated to be ca. 200 ns. The experiments were performed with a flow system employing a 0.5-mm quartz cell. Flow rates were from 1 to 10 mL/min and typically were around 5 mL/min. All of the solutions were deoxygenated by prolonged argon bubbling. The third laser harmonic (λ 355 nm; laser energy ~30 mJ/pulse, 20 Hz) was employed to excite the samples.

TR ESR spectra were recorded as absorption (intensity shown increasing above the base line) and/or emission (intensity shown decreasing above the base line) spectra.

The steady-state ESR spectra of the nitroxyls (microwave power ca. 2 mW, modulation amplitude varied from 0.1 to 1.0 G at a modulation frequency of 100 kHz, without significant variation in the form of the observed spectra) were recorded with the same Bruker spectrometer in the same cell as that employed for the TR ESR studies or were recorded on a Bruker ESR 300 as a first-derivative spectra and then numerically integrated as needed for comparison to TR ESR spectra.

2. Reagents. The ketones (Figure 1) benzophenone (BP, Aldrich), benzil (BZ, Aldrich), and 2-acetylnaphthalene (AN, Fluka) were used as received. Concentrations of BP and AN in homogeneous solutions were in the range 0.02–0.5 M, and the concentrations of BZ were in the range 0.005–0.01 M. TEMPO (Aldrich) and sodium dodecyl sulfate (SDS, Bio-Rad Laboratories) were recrystallized from diethyl ether. The solvents (benzene, acetonitrile, cyclohexanol, formamide, and 1-propanol) were all acquired from Fisher and used as received.

The structures and abbreviations of the various mono-, di-, tri-, and tetranitroxyl free radicals and ketones used are presented in Figure 1. Radicals I with different *n* (*n* = 1, 2, 4, 8, where *n* is the number of bridging methylene groups) are denoted as I$_n$. The following terminology has been employed: the symbol X represents the "templet" on which the stable spins are grafted to form a single molecule, and the symbol R represents a TEMPO function. A superscript immediately to the left of an R group (^{2}RX) refers to a noninteracting TEMPO moiety, i.e., one that spectroscopically behaves as a system with doublet multiplicity. A superscript to the immediate left of a parenthesis refers to the multiplicity of a polynitroxyl as deduced from its EPR spectrum; i.e., ^{3}(RXR) is a dinitroxyl that behaves spectroscopically as a system with the multiplicity of a triplet. It is important to note that a single structure may display different magnetic behavior under different experimental conditions (solvent and temperature) and that a single structure may simultaneously display spectroscopic evidence for two different multiplicities; i.e., the structure RXR may exist as a doublet state with two noninteracting spins (^{2}RX^{2}R) or as a triplet state [^{3}(RXR)], or as a simultaneous mixture of the two.

Radicals I$_n$ and II were synthesized[14] by the reaction of the appropriate diacid chlorides with 2,2,6,6-tetramethyl-4-hydroxy-*N*-1-oxyl (TEMPOL) in the presence of triethylamine in toluene. Radicals III and IV were synthesized[14] using PCl_3 and $SiCl_4$, respectively, as starting templates on which to graft the nitroxides.

The dinitroxyl I$_8$ and its mononitroxyl derivative (denoted ^{2}RXNH to indicate the replacement of a nitroxyl by an amine group) were synthesized by oxidation of the bis(tetramethylpiperidine)-1,10-decanoic ester (Tinuvin 770, Ciba-Geigy) as follows: to a 100-mL three-necked flask with reflux condenser,

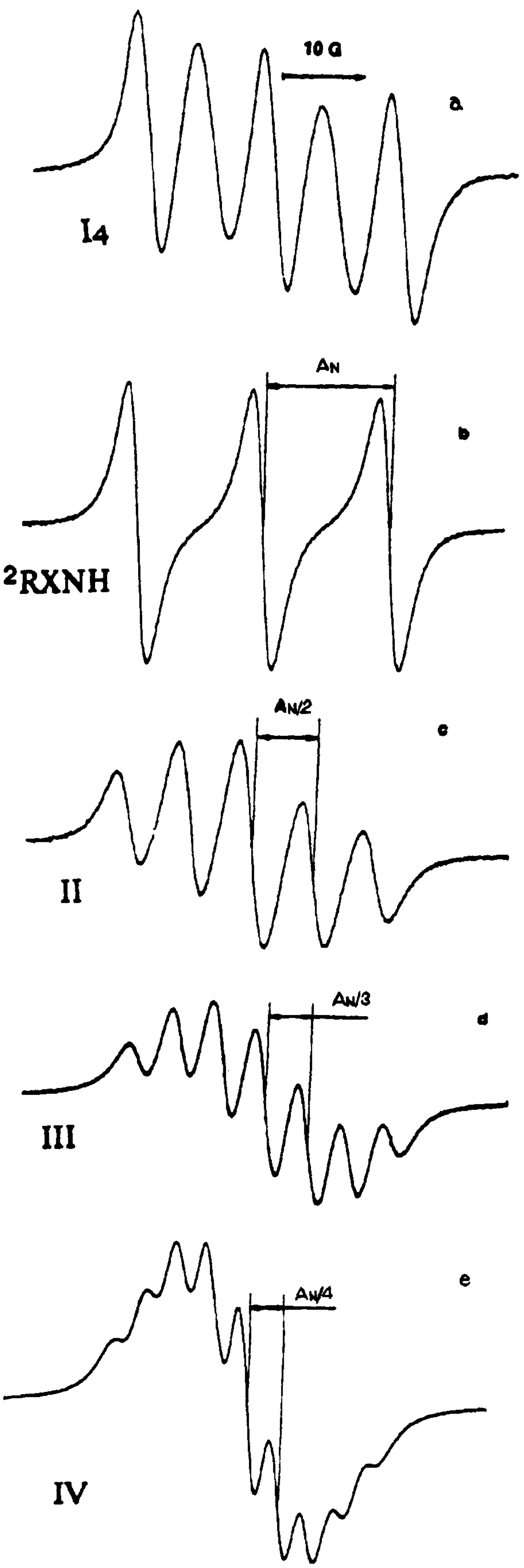


Figure 2. CW ESR spectra of polyradicals I_4 (a), ^{2}RXNH (b), II (c), III (d), and IV (e) in acetonitrile. The concentration of solutions was 1×10^{-3} M (a, c, d), 6.6×10^{-3} M (b), and 3×10^{-4} M (d).

TABLE I: Line Intensities and Line Positions in ESR Spectra of Polyradicals Found in the Strong Exchange Limit ($|J| \gg |A_N|$) and Designations of Polyradicals

polyradical	designation	line separation,[a] G	no. of lines	rel line intensities
II	^{3}(RXR)	$A_N/2 = 7.7$	5	1:2:3:2:1
III	^{4}(RXR$_2$)	$A_N/3 = 5.1$	7	1:3:6:7:6:3:1
IV	^{5}(RXR$_3$)	$A_N/4 = 3.8$	9	1:4:10:16:19:16:10:4:1

[a] Predicted from assuming $A_N = 15.3$ G for a nitroxyl monoradical. The hyperfine frequency is presented in gauss, where $a_N = A_N h/g\beta$.

stir bar, and additional funnel were mixed the following compounds at 273 K (ice cooling); dichloromethane (75 mL), 5.0 g of Tinuvin770, 1.5 g of *m*-chloroperbenzoic acid. The mixture was stirred for 1 h at 273 K and then refluxed for an additional hour. The mononitroxyl and dinitroxyl products were isolated using column chromatography employing activated silica gel (Fisher)/CH$_2$Cl$_2$ and neutral aluminum oxide (Brockman)/toluene.

Solutions of SDS micelles were prepared by adding sufficient deionized water to a stock solution of SDS to produce a concentration of 0.33 M. The concentration of micelles in such solutions can be estimated using literature values[15] of cmc = 8.2×10^{-3} M and aggregation number $N = 64$ as [M] = $\sim 5.0 \times 10^{-3}$ M. The reagents were also dissolved in micellar solutions in concentrations about 5×10^{-3} M.

Methods, Results, and Analysis

1. Steady-State ESR Spectra of Nitroxyls. Steady-state ESR spectra of all the mono- and polynitroxyls shown in Figure 1 were recorded in various solvents. Although the details of the ESR spectra depend upon solvent and polynitroxyl structures, the observed spectra are in agreement with the literature.[12] Figure 2 displays the ESR spectra of TEMPO and of the polyradicals I_4 and II–IV. The ESR spectra of these radicals in benzene and acetonitrile are very similar. The spectra for polyradicals II, III, and IV are in agreement with predictions for strong intramolecular spin exchange[12] (i.e., $|J| \gg |A_N|$, where $|J|$ is the magnitude of the exchange integral and $|A_N|$ is the magnitude of the hyperfine frequency). Table I summarizes the relative ESR line intensities and line positions predicted from the hyperfine constant for TEMPO for each of the possible multiplicities found in the strong exchange limit. The calculated hyperfine splitting constants of polyradicals (Table I) II, III, and IV show excellent agreement with the corresponding values measured from the spectra of Figure 2.

Although the observed spectrum of diradical I_4 does not agree precisely with that predicted for a triplet ESR spectrum, the spectrum can be described by the model developed in ref 12b, which assumes that the spectrum is a superposition of the spectra of a doublet (elongated diradical, ^{2}RX^{2}R, in a weak exchange, $|J| = 0$) and a triplet (contracted diradical, ^{3}(RXR), in a strong exchange, $|J| \gg |A_N|$) spectrum. The spectrum of I_4 also shows an alternating line width effect which, in the model, is the result of a molecular motion in the triplet conformation which modulates the exchange interaction.[12a] It is interesting to note that the spectrum of I_4 can be varied from a pure doublet spectrum (three ESR lines) to the doublet/triplet superposition spectrum in Figure 2a by varying the solvent system. (Although the spectrum of I_4 (Figure 2a) consists of five lines, their relative intensities are not those expected for pure triplet state (1:2:3:2:1); this is a result of the existence of some conformers of the dinitroxyl which are in a doublet form.[12b,c]) For example, I_4 shows a three-line spectrum in formamide [^{2}RX^{2}R] and a five-line spectrum in acetonitrile [^{3}(RXR)].

We now seek to calculate the fraction of the diradical I_4 in the doublet and triplet spin conformations. Let the fraction of molecules in the doublet conformation be f_d and the fraction of molecules in the triplet conformation be f_t. From the ESR spectrum of I_4 in Figure 2a and the theory of Parmon et al.,[12b] the ratio of lifetimes in the doublet, τ_d, and triplet, τ_t, conformations can be calculated through eq 1, where I_1 and I_2 are the

$$\tau_t/\tau_d = 3(I_2/I_1)/[2 - (I_2/I_1)] \qquad (1)$$

integrated intensities of the first and second hyperfine lines, respectively. The fractions of doublet and triplet can be calculated from the equations

$$f_d = 1/[(1 + (\tau_t/\tau_d)] \qquad (2a)$$

$$f_t = 1/[(1 + (\tau_d/\tau_t)] \qquad (2b)$$

The fractions of doublet and triplet conformations of I_4 were calculated to be $f_d = 0.24 \pm 0.05$ and $f_t = 0.76 \pm 0.05$, using eqs 1 and 2.

The ESR spectra of radicals I_1, I_2, and I_8 are similar to that of I_4; they can also be treated as a superposition of $^2RX^2R$ and $^3(RXR)$, and they show a similar solvent dependence.

The line widths of the ESR spectra of the stable radicals increase and the spectral resolution decreases with the (poly)radical concentration increase in the range of concentrations $C > \sim 1 \times 10^{-3}$ M as expected from the onset of increased spin exchange as a function of increased concentration.[16]

Both diradicals I_4 and II in SDS micelles and in cyclohexanol are in a weaker exchange than in homogeneous nonviscous solvents such as benzene or acetonitrile (Figure 2a,b); i.e., the systems can be characterized by $f_d \geq f_t$. The radical III in SDS micelles is in the limit of a weak exchange and shows three lines. In accordance with the notations employed, this trinitroxyl in a micellar system behaves as $^2RX^2R^2R$, but in benzene it behaves as $^5(RXR_2)$.

2. Photogeneration of Triplet States. Spin Sublevel Polarization. Photoexcitation of benzophenone (BP) (as well as benzyl (BZ) and 2-acetylnaphthalene (AN)) leads to the formation of polarization of the triplet sublevels,[1,17] as shown in eq 3, where

$$BP + h\nu \rightarrow {}^1BP^* \qquad (3a)$$

$${}^1BP^* \rightarrow {}^3BP^{*\#} \qquad (3b)$$

the symbol * stands for electronic excitation and the symbol # stands for non-Boltzmann population of the triplet spin sublevels in a magnetic field (i.e., electronic spin polarization). Polarization is generally thought to be generated in step 3b as the result of sublevel selective, spin–orbit induced $S_1 \rightarrow T_1$ intersystem crossing.[1-7] Spin–orbit interaction for $S_1 \rightarrow T_1$ in BP and AN generates spin-polarized triplets, $^3BP\#$ and $^3AN\#$, respectively, by selective population of the highest zero-field sublevel in the triplet (the zero-field splitting parameter $D < 0$),[1,18-21] whereas spin–orbit interaction for $S_1 \rightarrow T_1$ in BZ generates spin-polarized triplets $^3BZ\#$ by selective population of the lowest zero-field sublevel in the triplet (the zero-field splitting parameter $D > 0$).[18,22] Under the assumption of the triplet mechanism of CIDEP, these selective populations of sublevels lead to the expectation that electron spin polarization transfer from $^3BP\#$ and $^3AN\#$ will lead to emission of the acceptor radicals and that polarization transfer from $^3BZ\#$ will lead to enhanced absorption of the acceptor radicals.

In experiments with benzil special precautions were undertaken in order to prevent the formation and quenching of a higher excited triplet state T_n of this compound, which is known to have $D < 0$.[22] These precautions were the lowest possible laser energy and fastest flow rate.

We did not observe TR ESR spectra for benzyl ketyl or benzoyl radicals, and this also testifies to the absence of T_n population.[22]

3. Polarization under Interaction with Triplet States. Spin-polarized TR ESR spectra of mono- and polynitroxyls were observed following the photoexcitation of AN in various solvents and BP and BZ in non-hydrogen-donating solvents (acetonitrile and benzene) in order to avoid photoreduction. Figure 3 shows the TR ESR spectra for the four polyradicals, I_4 II, III, and IV, produced by benzophenone photoexcitation. It is important to emphasize that these spectra are in *emission* and are therefore completely due to electron-polarized species; i.e., are pure CIDEP spectra. In fact, control experiments show that *no* signals due to nitroxyls are observed for samples that lack ketones. Thus, we conclude that the observed spectra are due to polarized nitroxyls and that polarization results from interactions of nitroxyls with photoexcited ketones. Extremely rapid intersystem crossing of

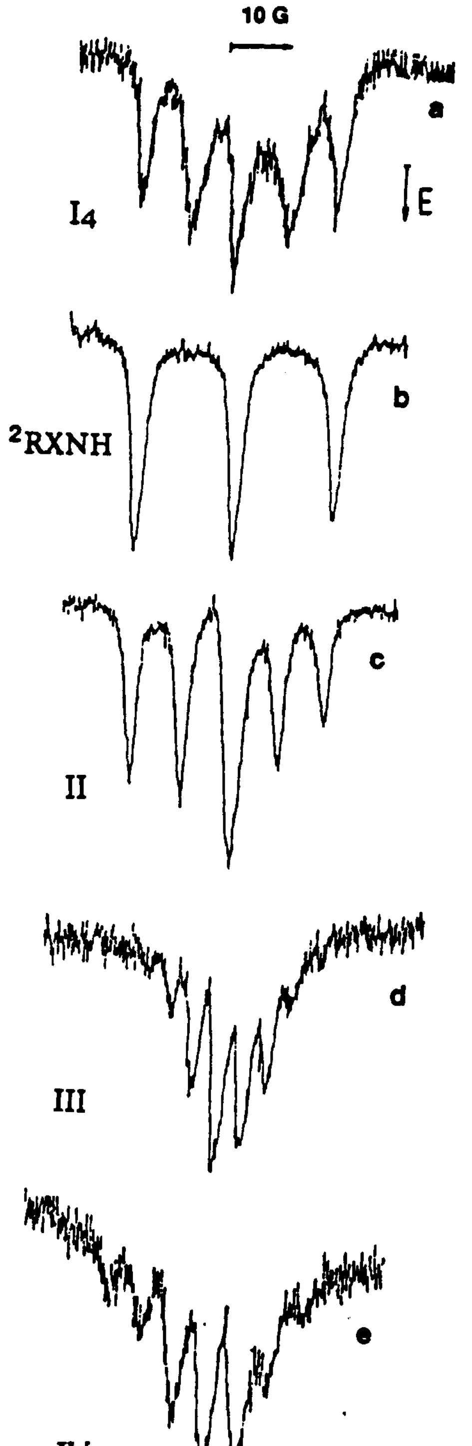


Figure 3. TR ESR spectra obtained under photolysis of BP with integration between 300 and 600 ns in the presence of polynitroxyls in benzene (a, c) and in acetonitrile (b, d, e). Concentration of solutions of I_4 (a), II (c), and III (d) was 1×10^{-3} M, that of IV (e) was 3×10^{-4} M, and that of ^2RXNH (b) was 6.6×10^{-3} M.

the aromatic singlets requires that it is the ketone triplets that are interacting with the nitroxyls.

In our TR ESR experiments we did not observe any measurable ESR signals from the normal Boltzmann population (poly)nitroxyl free radicals at concentrations less than ca. 5 × 10^{-3} M.

TR ESR spectra for I$_4$ II, III, and IV are all emissively polarized and display essentially the same spectral form (line patterns and relative line intensities) as those predicted in Table I and observed for the steady-state ESR spectra. (Note that although IV is expected to show a nine-line spectrum, the two outermost lines are lost in the noise and only the central seven lines are more intense than the noise in the observed spectrum.) For example, the TR ESR spectrum for I$_4$ is emissively polarized and displays the same line positions and relative intensities as the steady-state spectrum. Moreover, the fractions of doublet and triplet calculated from the spectrum for I$_4$ using eqs 1 and 2 are $f_d = 0.21 \pm 0.05$ and $f_t = 0.79 \pm 0.05$, respectively, which are essentially the same as the steady-state spectrum ($f_d = 0.24$ and $f_t = 0.76$, vide supra). Similar results were obtained with all of the triplet donors; i.e., the spectral parameters (line positions and relative intensities) of the observed TR ESR spectra were independent of the ketone employed for excitation. These results suggest a common source of interaction between ketone triplets and nitroxides which leads to the polarized nitroxides.

Although the ratio of lifetimes τ_d/τ_t can be determined from the ESR spectrum of diradical I$_4$, it is not possible to determine the lifetimes τ_d and τ_t independently.[12] However, the lifetimes must be greater than $1/A_N$ in order to be able to see the superposition of the doublet and triplet spectra.[12b] For the nitroxyl radicals A_N is ca. 50 MHz, which leads to a $1/A_N$ time of 20 ns. Therefore, doublet and triplet lifetimes of ca. 10–15 times $1/A_N$ are consistent with the observed superposition of spectra but would still be too short to allow for observation of the time evolution of the interconversion, since the predicted lifetimes are beyond or marginally within the TR ESR instrument response time. Currently, we are planning a FT-ESR experiment with a minimum response time of 80 ns in order to better probe this time regime.

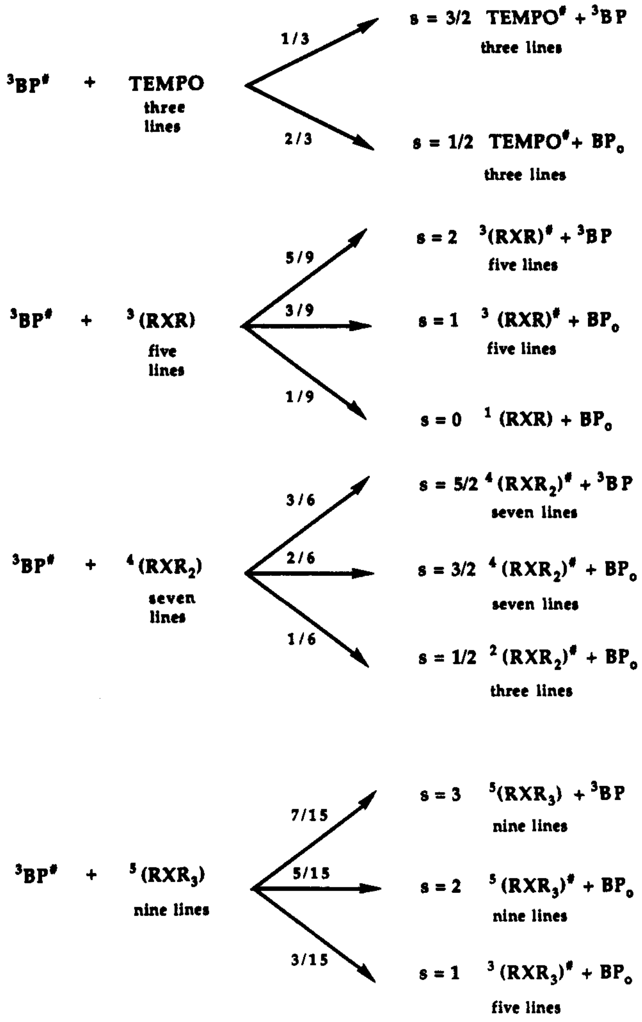
Emissively polarized TR ESR spectra of II were obtained under excitation of AN and BZ in SDS micelles. The quenching of ^{3}BZ in the presence of II occurred in micelles, because photoexcitation of BZ did not lead to the well-known CIDEP signals of alkyl radicals[13b] expected from hydrogen abstraction.

In general, the TR ESR spectra showed no time dependence of the spectral parameters, for sampling gates from ca. 200 ns (which is essentially the instrument response time) to 1.5–2.0 μs after the laser pulse, except for a uniform decrease in the overall intensity (due to T_{1e}). Even in solutions where molecular motion is hindered, e.g., SDS micelles and cyclohexanol, no variation in the form of the TR ESR spectra in time was observed.

In the case of ^{3}(RXR) systems the S–T splitting (J value) is relatively small ($|J| \ll kT$[12]), as are all J values of the polyradicals investigated. This condition leads to a finite population of the individual spin states of a given multiplicity, [$P(S)$], in the diradical or (poly)radical in a solution which is in accordance with the degeneracy of the corresponding spin state. For example, in the case of ^{3}(RXR) $P(1) = \sim 3/4$, $P(0) = \sim 1/4$; for ^{4}(RXR$_2$) $P(3/2) = \sim 2/3$, $P(1/2) = \sim 1/3$; and for ^{5}(RXR$_3$) $P(2) = \sim 5/9$, $P(1) = \sim 1/3$, $P(0) = \sim 1/9$. The existence of polyradicals in states with smaller than maximum spin multiplicity should be taken into consideration in interpreting the spectra (vide infra).

An interesting issue of concern to this investigation is whether there is a difference in the efficiency (or rate) of polarization generation for weakly and strongly coupled systems, e.g., ^{2}RX^{2}R vs ^{3}(RXR). In order to examine this issue experimentally, the efficiency of polarization generation of a mono- and dinitroxyl by benzophenone (BP) was investigated. Two structurally similar compounds, mononitroxyl ^{2}RXNH and dinitroxyl I$_8$, were selected as the polarization acceptors. TR ESR spectra were obtained under identical experimental conditions for BP with both ^{2}RXNH and I$_8$, except that the concentration of the dinitroxyl was one-half that of the mononitroxyl; i.e., the number of spins available to interact with BP triplets was approximately the same. After taking into account the fraction of dinitroxy molecules which are in the singlet state (ca. 17% = $f_t \times 1/4$) and the experimental uncertainty, the intensities of the emissively polarized TR ESR signals produced by excitation of BP were essentially the same for the mono- and dinitroxyl molecules. This result requires that there is no significant effect of strong and weak exchange on the rate and efficiency of polarization generation in the interaction of ^{2}RXNH and ^{3}(RXR) with benzophenone triplets and, by generalization, of doublets or states of higher multiplicity with triplets.

SCHEME I: Spin Statistics for Interaction of States of Different Multiplicity



The CIDEP TR ESR spectra of TEMPO produced by photoexcitation of any of the ketones investigated (BP, BZ, and AN) lead to three emissive line spectra of equal intensity (e.g., Figure 1b). Furthermore, the observed emissive spectrum of ^{2}RXNH is similar to that of TEMPO produced by the quenching of ^{3}BP. The quenching of ^{3}BP by mononitroxyls (see Scheme I) is almost diffusion-controlled.[9,11] The rate of possible hydrogen (or electron abstraction) reaction (eq 4) should be much less, and

$$^3\text{BP} + {}^2\text{RXNH} \rightarrow \text{BPH}^{\#\bullet} + {}^2\text{RXN}^{\#} \qquad (4)$$

in fact, no polarized ketyl free radicals were observed upon photolysis of BP in the presence of ^{2}RXNH. (We can probably assert that we do not see ^{2}RXN#, because this radical, which has

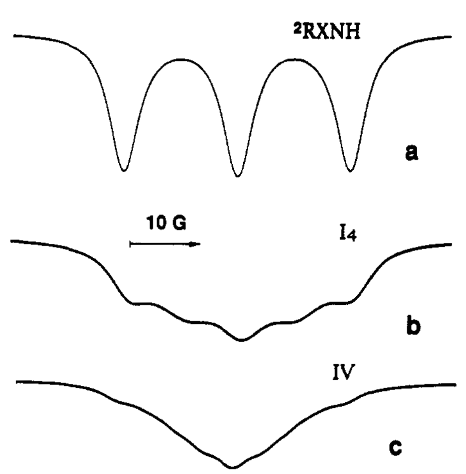


Figure 4. CW ESR spectra of solutions of ^{2}RXNH (a), I$_4$ (b), and of IV (c) shown in the integrated form for comparison of the CW and TR ESR spectra. The CW ESR of the same samples is presented as a first-derivative spectrum in Figure 2.

a similar structure to I$_8$, should have a spectrum of at least five components in acetonitrile, as I$_8$ has; vide supra.) The emissive components of a mononitroxyl (TEMPO) moiety were observed under polarization transfer to any dinitroxyl in a weak exchange (eq 5). Such behavior is quite reasonable for weakly interacting spin systems, i.e., ^{2}RXR^2.

$$^3\mathrm{BP}\# + {}^2\mathrm{RXR}^2 \rightarrow \mathrm{BP} + {}^{2\#}\mathrm{RXR}^2 \qquad (5)$$

The line widths (fwhm) in TR and CW ESR spectra of the same solutions of mononitroxyls taken in a concentration of $C < 10^{-3}$ M are in good agreement with experimental accuracy. The same conclusion can be reached from the data of refs 9 and 11, where quenching of photoexcited organic molecules by mononitroxyl ($C = 6 \times 10^{-4}$ M) was studied. However, in most cases TR ESR spectra of monoradicals and especially polyradicals ($C \geq 10^{-3}$ M) have better spectral resolution (smaller fwhm) than the corresponding CW ESR spectra of the same (poly)radical in the same solution of the same concentration presented in the integrated form. Figure 4 demonstrates three spectra of Figure 2 in the integrated form, i.e., spectra of mononitroxyl in relatively high concentrations and two spectra of polynitroxyls. Comparison of TR ESR and CW ESR spectra of (poly)nitroxyls in the same concentration in the same solvent in TR and CW experiments clearly shows that the fwhm in TR ESR spectra are smaller than in CW ESR spectra; cf. Figures 2b and 4a, Figures 2a and 4b, and Figures 2c and 4c. An increase of (poly)radical concentration leads also to a decrease of spectral resolution in TR ESR spectra. In particular, for the BZ*/TEMPO system, in the concentration of 6×10^{-2} M in acetonitrile, only a broad envelope, single emissive signal was observed.

The origin of the difference in spectral resolution of CW and TR ESR spectra of the same solutions of radicals is not very clear at present. At very short times of observation ($\sim 10^{-9}$ s) the opposite relation (i.e., *wider* TR ESR lines) between fwhm of CW and TR ESR spectra should be expected and observed in experiments due to the Heisenberg uncertainty principle and possibly due to Torrey oscillations.[3,7a]

4. Origin of CIDEP under Interaction of (Poly)nitroxyls with Triplet States. Mono- and polyradicals effectively quench triplet states.[1,2,7a,9,11,12b,23] The salient features of this investigation are that there is no significant difference in the efficiency or rate of generation (transfer) of spin polarization on ketone or nitroxyl structure. In particular, ketones with positive or negative zero-field parameters (BP and AN have $D < 0$ and BZ has $D > 0$) all induce emissive polarization in mono- or polynitroxyls. Furthermore, the form of the CIDEP spectrum observed by TR ESR is the same as that observed by steady-state ESR (except for slightly sharper line widths in the TR ESR spectra). Any mechanistic interpretation of the results must be able to explain these features of the observations. We consider two mechanisms to explain the observed CIDEP spectra in such triplet–doublet, triplet–triplet, triplet–quartet, and triplet–quintet pairs: (a) *polarization transfer* (by exchange or by dipole–dipole interactions) of electron-spin-polarized triplets to nitroxyls (ESPT) and (b) *polarization generation* by interaction of nonpolarized triplets and nitroxyls by a multiplet–multiplet radical pair mechanism analogous to the recently proposed doublet radical–triplet pair mechanism (RTPM).

a. Electron Spin Polarization Transfer (ESPT). The *first* mechanism we consider is the ESPT mechanism, which operates through an interaction (exchange or dipole–dipole) of a spin-polarized triplet state, produced by triplet sublevel selective intersystem crossing, with the mono- or (poly)radicals. This mechanism was suggested in refs 1, 2, 7a, and 11 to explain the observation of an emissively polarized mononitroxyl CIDEP spectrum under its interaction with ^{3}BP# and other photoexcited triplet molecules with $D < 0$. Scheme I presents possible polarization transfer steps to mono- and polynitroxyls and their statistical weights for the interaction of polarized triplet states (BP# is chosen as an example) with mono- and polyradicals (in the strong exchange limit), together with the number of lines expected in the species resulting from the transfer step and before relaxation. In actual cases (e.g., as found for I$_4$ in certain solvents), a mixture of two or more of the cases of Scheme I may be found to occur simultaneously. Polyradicals in nonzero spin states of lower multiplicity, namely ^{2}(RXR$_2$) and ^{3}(RXR$_3$) (see above), are believed to participate in ESPT in the same way as TEMPO and ^{3}(RXR). These reactions of ^{2}(RXR$_2$) and ^{3}(RXR$_3$) are omitted from Scheme I for brevity. Diamagnetic ^{1}(RXR) and ^{1}(RXR$_3$) cannot participate in ESPT.

In the case of BP, the T$_z$ sublevel (along the CO axis and highest energy zero-field level) is selectively populated by intersystem crossing from the S$_1$ state to produce spin-polarized ^{3}BP#. If ESPT between ^{3}BP# and a nitroxyl occurs, some of the excess spin population of the T$_z$ state of ^{3}BP# is transferred to the α (higher energy) spin level of the nitroxyl radical, and the overpopulation of this level results in the observation of emission in the observed TR ESR spectrum.[1,2,7a,11] The ESPT can occur via one of *two electron-exchange* mechanisms: electron exchange with triplet quenching to produce ground-state BP$_0$ or *spin exchange* without electronic quenching of the triplet state,[1,2,7a,11] as shown in Scheme I. Although dipole–dipole interaction is a possible mechanism for ESPT, it was shown to be ineffective in transfer between nitroxyls[1] and is assumed to be unimportant in the systems investigated here. In ESPT, independent of the interaction responsible for polarization transfer, it has been shown that the parameters which are conserved when the encounter complexes into products are the spin quantum numbers S and m_S.[2,11]

Although the ESPT mechanism is consistent with most of the results, it fails to explain the qualitative result that *emissive* polarization of (poly)nitroxyls is observed for interaction of the nitroxyls with the *absorptively* polarized triplet states of BZ. Another deficiency of the ESPT mechanism is quantitative and is related to the requirement of very fast polarization transfer, before relaxation of triplet sublevels, which is expected to occur with time constants of the order of 10^8–10^9 s^{-1}.[1] To be competitive with such rapid relaxation, concentrations much higher than those employed (ca. 10^{-3} M, corresponding to a maximum pseudo-first-order quenching rate of ca. 10^6–10^7 s^{-1}, even for diffusion-controlled polarization transfer) are needed for efficient capture of the triplet polarization. Moreover, attempts to intercept the initial absorptive polarization of BZ*# with high concentrations of (poly)nitroxyl were unsuccessful; emissive signals of (poly)-nitroxyl were observed for concentrations up to 0.1 M (poly)-

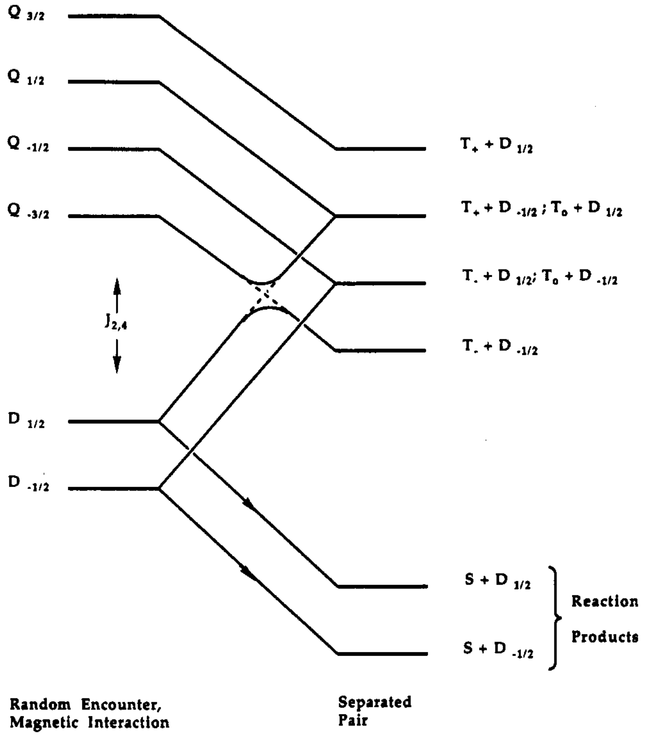


Figure 5. Schematic representation of state mixing under triplet–doublet encounter in a magnetic field. After refs 8a and 9a. Only one avoided crossing region is shown; this nonadiabatic transition provides the action of RTPM.

nitroxyl. Finally, experiments with the quenching of ^{3}BZ in micelles, where an enhanced interaction of reagents occurs, by dinitroxyl II still led to emissive signals of polarized II (see section 3).

It is worthwhile to mention that BZ has fluorescence.[22] Under excitation of solutions of BZ (1×10^{-3} M) in acetonitrile with 355-nm light as in the TR ESR experiments, we observed fluorescence with λ_{max} 510 nm. (The fluorescence, and not phosphorescence, was observed, because deoxygenation of a solution led to a minor increase in the signal intensity, i.e., up to 1–2%). Addition of TEMPO in concentrations up to 5×10^{-3} M leads to quenching of the luminescence intensity up to 15%. This quenching most probably results in the increase of the triplet-state quantum yield.[22] Quenching of a *singlet* state by TEMPO could lead to *absorptive* signals in a TR ESR spectrum of this radical,[9] but was not observed. So, it is impossible to explain the emissive signals of (poly)nitroxyls observed under interaction with photoexcited singlet BZ as the mechanism of the observed CIDEP.

We note that Scheme I ignores interconversions between states of different multiplicity during encounters. If such interconversions are taken into account, a second mechanism for polarization to the nitroxyl radicals is available and can readily explain all of the observations.

b. Polarization Generation Mechanisms. Since the ESPT mechanism cannot explain all of the results, we consider a *second* mechanism involving interactions of radical–triplet pairs (RTPM), in which the interacting triplet is *unpolarized.* In this mechanism *polarization is generated by the triplet–radical interaction.* Figure 5 illustrates the basic idea of the proposed RTPM, which has similarities to the S–T$_-$ mechanism for creating CIDEP in radical pairs (RP).[8–11] It follows from Figure 5 that, under the assumption that upon formation of collision complexes between a doublet radical and a triplet, the probabilities of population of all quartet (Q) and doublet (D) states are possible and determined only by statistical considerations, the $D_{1/2}$ state of the (nitroxyl) free radical, which separates after an encounter with a triplet state becomes overpopulated independent of any polarization of the triplet state, because of selective formation of the ground-state triplet through encounters involving $D_{-1/2}$ states of the doublet radical. This generation of spin polarization is indicated by the arrow in Figure 5, which shows the $T_- + D_{-1/2}$ pair being selectively depleted by passing adiabatically through an avoided surface crossing (in zero order to $Q_{-3/2}$) to an encounter complex which can deactivate to a $S + D_{-1/2}$ state. This process for depleting $D_{-1/2}$ states is not balanced by the corresponding depletion of $D_{1/2}$ states through $T_+ + D_{1/2}$ interactions, because the latter pair does not experience a surface crossing in the collision complex ($T_+ + D_{1/2} \rightarrow Q_{3/2}$). This mechanism for overpopulation of the $D_{1/2}$ levels of the nitroxyl leads to net emissive CIDEP signals and is independent of the sign of D.[8–10]

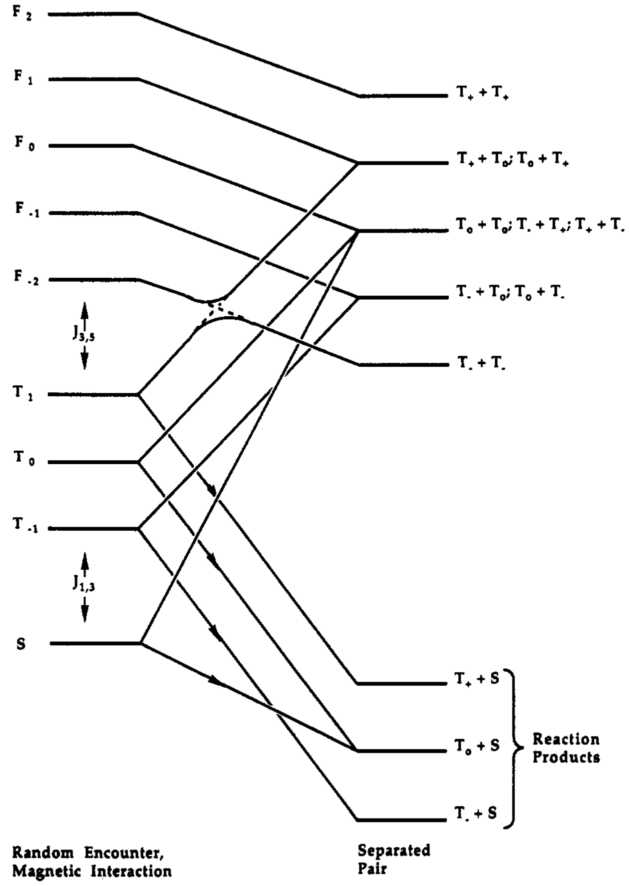


Figure 6. Schematic representation of state mixing under triplet–triplet encounter in a magnetic field. Only one avoided crossing region is shown; this nonadiabatic transition provides the action of TTPM.

In order for this mechanism to operate, some magnetic interaction (e.g., zero-field or hyperfine coupling) must be effective in mixing $D_{1/2}$ and $Q_{-3/2}$ states in the collision complex, i.e., in the region of nonzero exchange interaction $J_{2,4}$ between quartet and doublet states. In addition, we assume a negative sign of the $J_{2,4}$ and fast deactivation of the $D_{\pm 1/2}$ states of the encounter complexes.

The *emissively* polarized signals of TEMPO were observed under the interaction of *absorptively* polarized ($D > 0$) triplet diphenylmethylene with TEMPO.[7b] The possible reason for such an observation can be the action of RTPM.

We can apply similar considerations to cases involving the interaction of triplet ketones with nitroxyls of higher multiplicity, i.e., for triplet–triplet, triplet–quartet, and triplet–quintet interactions. Thus, as a specific example, we interpret our results in terms of a novel triplet–triplet pair mechanism (TTPM, Figure 6), which can be readily extended to include triplet–quintet and triplet–septet mechanisms. Encounters between two triplets produce a quintet (we use the symbol F for a quintet to avoid confusion with the symbol Q which has already been used for a quartet), a triplet (T), and a singlet (S) for a total of nine possible spin states.[24] The mixing of the quintet (F) and triplet (T) states of pairs in the region of nonzero negative $J_{3,5}$ should lead to preferential population of T_+ and T_0 states of the ^{3}(RXR) dinitroxyl which separates after the encounter. Under the usual assumption of a negative value for exchange $J_{2,4} < 0$ (Figure 6), this mechanism predicts the emissive mode of CIDEP of ^{3}(RXR), independent of the sign of D, which is what is observed. These considerations lead to agreement with the observations and can be extended to triplet–quartet interaction, provided that $J_{4,6} < 0$ (quenching of triplet states by ^{4}(RXR$_2$)) and triplet–quintet interaction provided $J_{5,7} < 0$ (quenching of triplet states by ^{5}(RXR$_3$)), etc.

We must note that the sign of $J_{2,4}$ ($J_{4,6}$, etc.) is not known from our experiments, and our experiments do not determine the sign of this interaction. Indeed, if one assumes that $J_{2,4} > 0$, then ZFS-induced transitions between $Q_{3/2}$ and $D_{-1/2}$ (cf. Figure 5) will lead to the same emissive pattern of a mononitroxyl in RTPM.[8,10] Quite similarly, ZFS-induced transitions between F_2 and T_{-1} will lead to an emissive pattern in the CIDEP spectrum of ^{3}(RXR) provided $J_{3,5} > 0$. Theoretical or any experimental estimations of sign and magnitude of exchange interaction in such systems are important for validation and further development and tests of the proposed novel mechanisms of CIDEP.

The hyperfine coupling (HFC) induced Q–T interconversion can contribute to RTPM, leading to a hyperfine-dependent (E*/A) pattern in the TR ESR spectra of nitroxyls.[9] The relative contribution of a HFC mechanism becomes larger in the case of relatively small rapidly rotating molecules, such as acetone and phenazine, because such rotation partially averages out the ZFS of triplet and therefore reduces its ability to provide the necessary magnetic interaction in the collision complexes. However, under the present study of molecules or larger size (volume) such as BP, AN, and BZ, the observed TR ESR spectra of mononitroxyls show components of equal size and symmetry (Figure 3) consistent with a negligible contribution from HFC interconversions, which would add an unsymmetrical character (E/A or A/E) to the observed spectra. The absence of significant hyperfine contributions was also concluded from the experimental data in refs 7a and 11 on CIDEP involving the interaction of ^{3}BP# with mononitroxyls.

It appears that the RTPM and TTPM for generation of net CIDEP play a dominant role for the interaction of nonpolarized triplet states with $D > 0$ with mono- and dinitroxyls. At the same time, these mechanisms do not provide a compelling basis for total rejection of the mechanism of ESPT discussed above for the triplet possessing $D < 0$. The analysis of many CIDEP observations showed the necessity to employ two or more mechanisms to explain the experimental data.[1–6] In particular, in the case of ^{3}BP#, which is strongly polarized,[20] the net polarization transfer according to reactions presented in Scheme I seems to be quite possible. For triplet states with different signs of D the two mechanisms can act in the same or opposite directions, and for the case of a positive D the ZFS mechanism for creating polarization prevails.

It has been found recently that an increase in the solvent viscosity leads to an increase in the magnitude of TR ESR signals under the quenching of the excited states by nitroxyls.[9c] This experimental observation is reasonably explained by the RPTM action.[9c] At the same time the increase in solvent viscosity should lead to a decrease in the triplet T_{1e}[1] and can lead to an increase in the magnitude of the signal according to a ESPT mechanism.

Conclusions

The present work demonstrates that the interactions of ketone triplets (benzophenone, 2-acetophenone, and benzil) and mono-, di-, tri-, and tetranitroxyls produces exclusively emissive polarization of the nitroxyls which produce CIDEP spectra that are readily detected and investigated by TR ESR. It was established that, in several solvents and in a micellar media, the TR ESR spectra of (poly)nitroxyls obtained by polarization transfer from triplet states are very similar in form to the CW ESR spectra of the same (poly)nitroxyls in the same solvent in the same concentration.

No significant difference in the efficiency of polarization transfer to mono- and polynitroxyls was observed; i.e., the rate of spin polarization transfer to polynitroxyl is proportional to the total number of spins in solution and is not significantly affected by the (spectroscopic) multiplicity of the polynitroxyl.

Within the time window of the TR ESR experiments ($\sim 10^{-7}$–10^{-6} s), no detectable variation in the form of the TR ESR spectra of the polynitroxyls was observed. In other words, no polynitroxyl, in particular dinitroxyl, dynamics were observed. If polarization of a single nitroxyl moiety, within a polynitroxyl, occurs by interactions with a triplet, the relaxation of the system to the strong exchange limit is faster than the time resolution of the experiment.

TR ESR spectra of dinitroxyl with a small exchange interaction ($|A_N| \gg |J|$) obtained under a polarization transfer from triplet or doublet are quite similar to those of mononitroxyl and to the corresponding CW ESR spectra of a polyradical as a polarization acceptor.

Of the two conventional CIDEP mechanisms which can lead to net polarization of the nitroxyl systems, the RPTM with an appropriate extension to the higher multiplicity nitroxyls is consistent with all of the experimental observations, under the assumption of a negative value of the exchange interaction during encounters of triplet ketones and mono- or polynitroxyls.

Although our experiments provide no evidence for ESPT from electron-spin-polarized triplets, it is possible that the proper experiments for observation of this mechanism have not been performed. In order to intercept the polarized triplet before it relaxes to the Boltzmann distribution by spin–lattice interactions, a very high concentration of nitroxyl is required. Assuming a diffusional quenching constant of ca. 10^9 M^{-1} s^{-1} for polarization transfer and a spin–lattice relaxation of ca. 10^9 s^{-1} for the triplet, a concentration of 1 M nitroxyl is required for ca. 50% quenching! At these concentrations the nitroxyl spectra are dominated spin-exchange effects. However, we note that it may be possible to find a system where at low concentrations of nitroxyl an emissive CIDEP is observed and that the *integrated* intensity of the signal first increases, then plateaus, and then increases as a function of the nitroxyl concentration. This would occur if at low concentrations the RTPM dominated and then saturated as all of the nonpolarized triplets were quenched. At still higher concentrations polarized triplets would be quenched increasing the observed polarization (if the inherent polarization available for transfer is greater by a pure ESPT mechanism). We also note that our attempts to organize a spin donor and acceptor (nitroxyl) by coadsorption in a micelle failed to provide evidence for absorptive ESPT in the case of BZ and II. Finally, we note that in the cases investigated (I_4 and II) the dinitroxyl tends to experience weaker exchange in micelles than in homogeneous solutions.

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References and Notes

(1) Jenks, W. S.; Turro, N. J. *Res. Chem. Intermed.* **1990**, *13*, 237.

(2) Obi, K.; Imamura, T. *Rev. Chem. Intermed.* **1986**, *7*, 225.

(3) McLauchlan, K. A. In *Lasers in Polymer Science and Technology: Applications*; Fouassier, J.-P., Rabek, J. F., Eds.; CRC Press: Boca Raton, FL, 1990; Vol. 1, p 259.

(4) (a) Adrian, F. J. *Res. Chem. Intermed.* **1991**, *16*, 99. (b) Adrian, F. J. *Rev. Chem. Intermed.* **1986**, *7*, 173.

(5) Trifunac, A. D.; Lawler, R. G.; Bartels, D. M.; Thurnauer, M. C. *Prog. React. Kinet.* **1986**, *14*, 43.

(6) Steiner, U. E.; Wolff, H. J. In *Photochemistry and Photophysics*; Rabek, J. F., Ed.; CRC Press: Boca Raton, FL, 1991; Vol. 14, p 1.

(7) (a) Jenks, W. S. Ph.D. Thesis, Columbia University, New York, NY, 1991. (b) Jenks, W. S.; Turro, N. J. *Tetrahedron Lett.* **1989**, *30*, 4469.

(8) (a) Blätter, C.; Jent, F.; Paul, H. *Chem. Phys. Lett.* **1990**, *166*, 375. (b) Blätter, C.; Paul, H. *Res. Chem. Intermed.* **1991**, *16*, 201.

(9) (a) Kawai, A.; Okutsu, T.; Obi, K. *J. Phys. Chem.* **1991**, *95*, 9130. (b) Kawai, A.; Obi, K. *J. Phys. Chem.* **1992**, *96*, 52. (c) Kawai, A.; Obi, K. *J. Phys. Chem.* **1992**, *96*, 5701.

(10) Shushin, A. I. In *Magnetic Field and Spin Effects in Chemistry and Related Phenomena*; Book of Abstracts of International Symposium 26–31 July 1992; Konstanz, FRG, 1992; p 6.

(11) Imamura, T.; Onitsuka, O.; Obi, K. *J. Phys. Chem.* **1986**, *90*, 6741.

(12) (a) Luckhurst, G. R. In *Spin Labeling. Theory and Applications*; Berliner, L. J., Ed.; Academic: New York, 1976; Vol. 6, p 133. (b) Parmon, V. N.; Kokorin, A. I.; Zhidomirov, G. M. *Stable Biradicals*; Nauka Publishers: Moscow, 1980; 240 pp (in Russian). (c) Parmon, V. N.; Kokorin, A. I.; Zhidomirov, G. M. *Zh. Struct. Khim.* **1977**, *18*, 132.

(13) (a) Doubleday, C.; Turro, N. J.; Wang, J.-F. *Acc. Chem. Res.* **1989**, *22*, 199. (b) Closs, G.; Forbes, M. D. E.; Piotrowiak, P. *J. Am. Chem. Soc.* **1992**, *114*, 3285.

(14) (a) Rozantsev, E. G.; Scholle, V. D. *Synthesis* **1971**, 190. (b) Glarum, S. H.; Marshall, J. H. *J. Chem. Phys.* **1967**, *47*, 1374.

(15) (a) *Surfactant Science Series*; Lucassen-Reynders, E. H., Ed.; Marcel Dekker: New York, 1981; Vol. 11. (b) Mukerjee, P.; Mysel, K. J. *Critical Micelle Concentrations of Aqueous Surfactant Systems*; NSRDS-NBS 36, 1971.

(16) Molin, Yu. N.; Salikhov, K. M.; Zamaraev, K. I. *Spin Exchange. Principles and Applications in Chemistry and Biology*; Springer: Berlin, 1980; p 242 ff.

(17) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin: Menlo Park, CA, 1978.

(18) Grant, A. I.; McLauchlan, K. A. *Chem. Phys. Lett.* **1983**, *101*, 120.

(19) Akiyama, K.; Tero-Kubota, S.; Ikegami, Y.; Ikenoue, T. *J. Am. Chem. Soc.* **1984**, *106*, 8322.

(20) Hayashi, H.; Sakaguchi, Y.; Murai, H.; I'Haya, Y. J. *J. Phys. Chem.* **1986**, *90*, 4403.

(21) Akiyama, K.; Kaneko, A.; Tero-Kubota, S.; Ikegami, Y. *J. Am. Chem. Soc.* **1990**, *112*, 32970.

(22) (a) Mukai, M.; Yamauchi, S.; Hirota, N. *J. Phys. Chem.* **1992**, *96*, 3305. (b) Mukai, M.; Yamauchi, S.; Hirota, N. *J. Phys. Chem.* **1989**, *93*, 4411. It is worthwhile to note that if T_n would be populated by a $T_1 + h\nu \rightarrow T_n$ process, a positive sign of D should be preserved in T_n; see ref 22a.

(23) (a) Lymar, S. V.; Kokorin, A. I.; Parmon, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 2616. (b) Borisevich, Yu. E.; Kuzmin, V. A.; Kokorin, A. I.; Sennikov, G. P.; Novozhilova, G. A.; Shapiro, A. B. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 2019.

(24) (a) Lendi, K.; Gerber, P.; Labhart, H. *Chem. Phys.* **1976**, *18*, 449. (b) Closs, G. L. *J. Am. Chem. Soc.* **1971**, *93*, 1546. (c) Schulten, K. *J. Chem. Phys.* **1984**, *80*, 3668.