On the Manifestation of S−T₋ Transitions in Weak Magnetic Fields. CIDNP for Radical Pairs with Large HFI Constants

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The CIDNP effects observed in photolytic reactions of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMBDPO) and benzoylphosphonic acid dimethyl ester (BDMP) in organic solvents of different viscosities are determined by $S-T_-$ transitions that occur in the region of energy levels crossing. An analytical expression is proposed for calculation of the CIDNP effects at weak magnetic fields, which takes into account the $S-T_-$ transitions due to energy levels crossing. The experimental data are compared to the results obtained by the numerical solution of the stochastic Liouville equation (SLE) for a microreactor model. The parameters that affect the efficiency of the $S-T_-$ transitions are discussed.

Introduction

Calculations of CIDNP effects at weak magnetic fields have received considerable attention.[1] It is shown that in homogeneous solutions the basic contribution to the polarization is made by the singlet−triplet transitions that occur after long diffusion wandering, i.e., when the exchange interaction is nearly zero. In such systems, changes in signs of CIDNP field dependencies (sometimes repeated) are usually explained by mutual effects of nuclei.[2] By contrast, in RPs of restricted mobility (biradicals, micellized RPs) the main contribution to the polarization is made by singlet−triplet transitions that occur in the region of energy levels crossing.[3,4] In this region, the lifetime of RPs and hence the efficiency of singlet−triplet transitions increase.

However, in some cases, the $S-T_-$ transitions proceeding in the region of energy levels crossing are likely in homogeneous solutions as well. These are the cases where hyperfine interaction (HFI) constants are rather large. Since the efficiency of these transitions increases as the square of the HFI constant,[2,5] at large constants they become significant.

At the same time, in some reactions,[1,3] at weak magnetic fields the observed CIDNP effects were explained by $S-T_-$ transitions at relatively small HFI constants of the radical pairs. However, in almost all cases, the resulting radicals exhibit considerable additional HFI constants of the neighboring nuclei, which make certain contributions to the total effects.

The radical pairs that involve diphenylphosphonyl and dimethoxyphosphonyl radicals, i.e., radicals with the large HFI constants of the phosphorus nuclei (∼37.5 and 70 mT, respectively), and insignificant constants of other nuclei (<0.01 mT,[6] 6 × 0.03 mT[7] for the ^{1}H nuclei, respectively) are convenient objects for the studies of the CIDNP formed due to the $S-T_-$ transitions proceeding in the region of energy levels crossing. In this work, to study the CIDNP effects in systems with large HFI constants we used (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMBDPO) and benzoylphosphonic acid dimethyl ester (BDMP).

The possibility of manifestation of the $S-T_-$ transitions that occur in the region of energy levels crossing in homogeneous solutions was investigated both theoretically and experimentally.

Experimental Section

(2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (**Ia**) (from BASF) was recrystallized from hexane. Benzoylphosphonic acid dimethyl ester (**Ib**) was synthesized as described in ref 17: bp 131−132 °C (3 Torr); ^{13}C{^{1}H} (75 MHz, CDCl$_3$) δ 198.2 (d, $^1J_{C-P} = 173$ Hz, C=O), 135.4 (d, $^2J_{C-P} = 57$ Hz, C-*ipso*), 134.9 (s, C-*para*), 129.7 (d, $^3J_{C-P} = 1.5$ Hz, C-*ortho*), 128.0 (d, $^4J_{C-P} = 0.8$ Hz, C-*meta*), 54.1 (d, $^3J_{C-P} = 8$ Hz, CH$_3$). All solvents were received from Reachim, Russia. Benzene was washed with concentrated H_2SO_4, dried over $CaCl_2$, and distilled. The ester was washed with concentrated H_2SO_4, a solution of NaOH, and water; then it was dried over KOH and sodium and distilled. Acetonitrile was stirred with $KMnO_4$ (0.1 g/L) for 30 min, filtered, distilled, filtered through an Al_2O_3 column, distilled over P_2O_5, and distilled over CaH_2. Cyclohexane and 95% ethanol were purified by distillation.

In CIDNP experiments, 0.0025 M solutions of TMBDPO and 0.005 M solutions of BDMP were used.

The experimental CIDNP setup was described elsewhere.[18] The reaction mixture was irradiated by laser pulses (ELI, Estonia) (308 nm, 20 Hz, energy 25−40 mJ/pulse, pulse duration 20 ns) in the field of a homemade magnet. A flow system was used to transfer the irradiated mixture to the probe of a Bruker MSL 300 NMR spectrometer. The transfer time was 1 s, the residence time being about 5 s.

Results

As is known, the photolysis of TMBDPO in both homogeneous[8−11] and micellar[12,13] solutions involves the C−P bond cleavage from a triplet molecule to form trimethylbenzoyl−diphenylphosphonyl radical pairs with the only HFI constant (37.5−38.3 mT[14,15]) at the ^{31}P nuclei. The radicals arising in the photolysis of TMBDPO (**Ia**) recombine in solvent cages to yield the original compound and [(2,4,6-trimethylbenzoyl)oxy]-diphenylphosphine (**IIa**) as well as to react in the solution after escaping from the cages to give various products depending on the solvent/substrate ratio (Scheme 1).[8−11] For BDMP, there is no reliable evidence of rapid intersystem crossing and α-cleavage from the triplet state. Moreover, it is shown[16] that in the photolysis of benzoylphosphonic acid diethyl ester (X = OEt; see Scheme 1) the α-cleavage is an insignificant process. At the same time, the photolysis of (2,4,6-trimethylbenzoyl)-phosphonic acid dimethyl ester involves α-cleavage,[8,16] which

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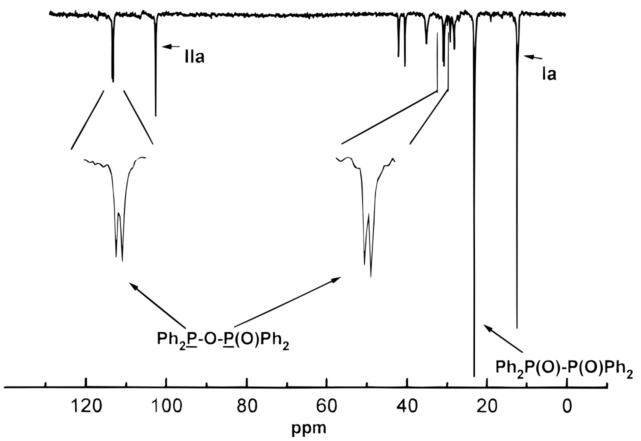
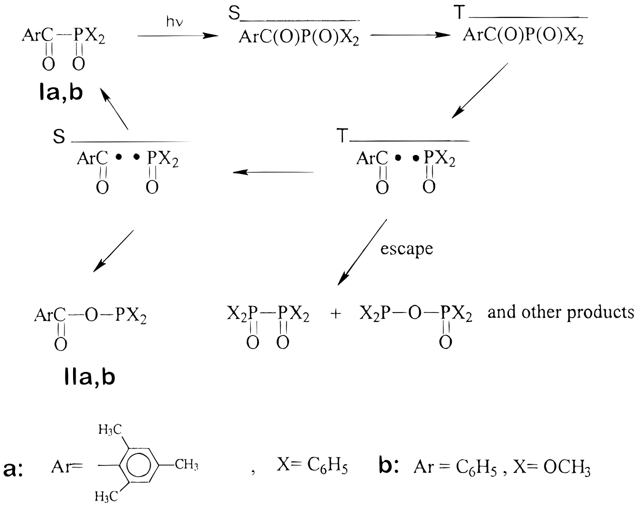


Figure 1. CIDNP ^{31}P-NMR spectrum (one scan) obtained upon TMBDPO photolysis in benzene.

SCHEME 1



occurs mainly from the triplet state and gives rise to the corresponding radicals. Thus, one might expect that in the case of BDMP the reaction proceeds partly through α-cleavage from the triplet state.

Figure 1 shows the ^{31}P-NMR–CIDNP spectrum detected in the photolysis of TMBDPO in benzene at a magnetic field of 60 mT. The main peaks were assigned using the data of Kolczak et al.[19] It can be seen that in-cage and escape products show emissive signals. It should be noted that the products arising in the photolysis of TMBDPO in ether, acetonitrile, cyclohexane, 95% ethanol, and aqueous solutions of sodium octyl and dodecyl sulfate (SDS) micelles[13] also exhibit emission.

Figure 2 presents the CIDNP field dependencies obtained in the photolysis of TMBDPO in ether, acetonitrile, cyclohexane, 95% ethanol, and benzene and detected by the ^{31}P-NMR signals of TMBDPO. It can be seen that the curves have pronounced maxima in the region 50–70 mT; for rather viscous solvents, the maxima are slightly shifted toward the high fields. The high-field portions of the curves suggest a distinct correlation between the solvent viscosity and emission-to-adsorption transition point.

In the photolysis of BDMP (**Ib**) in acetonitrile, all products also exhibit emissive CIDNP. Figure 3 shows the CIDNP field dependence detected by the NMR signal of the original compound in the photolysis of BDMP in acetonitrile. Since the HFI constant (70 mT[7]) of the dimethoxyphosphonyl radicals is large in comparison with the HFI constant for diphenylphosphonyl radical (37.5 mT), the maximum of this field dependence is significantly shifted to high fields (90 mT).

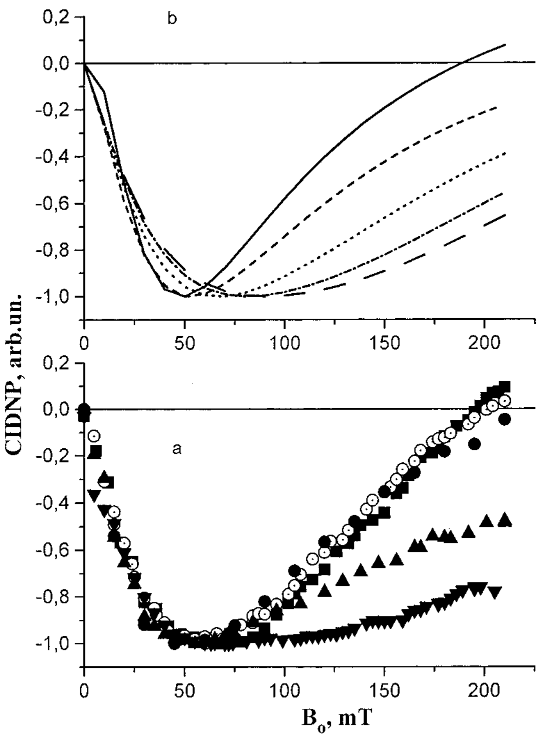


Figure 2. (a) Experimental CIDNP field dependencies for the photolysis of TMBDPO: (▼) in 95% ethanol; (▲) in cyclohexane; (●) in benzene; (○) in acetonitrile; (■) in ether. (b) CIDNP field dependencies calculated by numerical solution of SLE: (— —) in ethanol; (- -) in cyclohexane; (•••) in benzene; (- - -) in acetonitril; (—) in ether. Calculation parameters: $g_1 = 2.004$, $g_2 = 2.0006$, $A = 37.5$ mT, $J_0 = -4.4 \times 10^{10}$ rad/s, $\lambda = 0.8$ Å, $R = 7$ Å, $L = 400$ Å, $k_{\mathrm{scv}} = 5 \times 10^6$ s^{-1}, $k_S\tau = 7$.

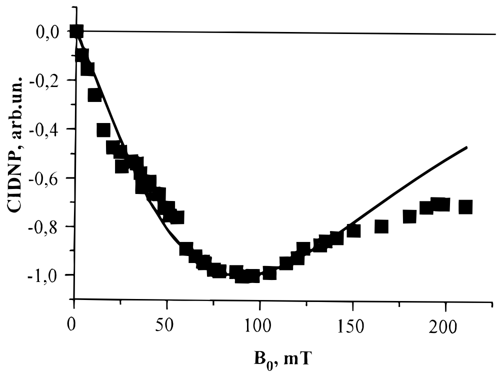


Figure 3. Experimental (■) and calculated (—) by numerical solution of SLE CIDNP field dependencies for the photolysis of BDMP in acetonitrile. Calculation parameters: $g_1 = 2.0018$, $g_2 = 2.0008$, $A = 70$ mT, $J_0 = -4.4 \times 10^{10}$ rad/s, $\lambda = 0.8$ Å, $R = 6$ Å, $L = 400$ Å, $k_{\mathrm{scv}} = 5 \times 10^6$ s^{-1}, $k_S\tau = 1$.

We estimated the difference in the absolute values of CIDNP effects of TMBDPO in different solvents. In ethanol, the CIDNP amplitude is approximately 10 times higher than that in diethyl ether and about 100 times less than that in the micellar solution. Our previous investigations of the photolysis of dibenzyl ketone (DBK) with carbonyl ^{13}C in benzene and in SDS micelles (HFI constant of the resulting benzoyl radical 12.4 mT)[20] have shown that in micelles the CIDNP effect is 3 orders of magnitude larger than that in benzene, the sign of polarization being opposite.

Theory

The CIDNP effect is characterized by the average value of the operator $\hat{I}_z$ of the nuclear spin in recombination products.

The average value $\langle \hat{I}_z \rangle \equiv \langle m \rangle$ can be expressed in terms of the recombination probability W_m of RP subensembles with different configurations of the nuclear spins

$$\langle m \rangle = \sum_m m W_m \tag{1}$$

For an RP with one magnetic nucleus with the spin $I = {}^1/_2$, there are two subensembles and $m = \pm{}^1/_2$.

As is known, the recombination probabilities of different RP subensembles depend on the spin state of the RP precursors and on the reactive—singlet or triplet—state. In our case, where the RPs are generated in the triplet state and recombine from a singlet state, the recombination probability W_m can be written as follows:[21]

$$W_m = \frac{1}{3}\frac{U_o(\tau_p - \tau_m)}{1 + U_0\tau_m} \tag{2}$$

where U_0 is the quasi-unimolecular rate constant of recombination from the singlet state, τ_m is the average residence time of radicals in the singlet state in the reaction zone at a given nuclear spin configuration m on condition of the start from the reaction zone in the singlet state, and τ_p is the average residence time of radicals in the reaction zone irrespective of their spin state.

The times τ_m and τ_p depend on the kinematics of the relative motion of radicals in the pair and on the effective shape of the reaction zone. The time τ_m also depends critically on the RP spin evolution rate. The value of τ_m can be expressed through the convolution of the element of the Green matrix $\hat{\hat{\varphi}}(\vec{q},\vec{q}',t)$ that specifies both the kinematics of the relative motion of radicals in the configuration space ($\vec{q}$ is the configuration space coordinate), and the spin evolution of the pair in the singlet—triplet basis set with the spin evolution absent, $\tau_m = \tau_p$:

$$\begin{gathered}\tau_m \equiv (\hat{\hat{g}})_{s_m s_m, s_m s_m} \\ \hat{\hat{g}} = \int_0^\infty \psi(\vec{q})\, \hat{\hat{\varphi}}(\vec{q},\vec{q}',t)\, \psi(\vec{q}')\, \mathrm{d}t\, \mathrm{d}\vec{q}\, \mathrm{d}\hat{q}'\end{gathered} \tag{3}$$

where $\psi(\vec{q})$ is the normalized function of the effective shape of the reaction zone.

The matrix $\hat{\hat{\varphi}}(\vec{q},\vec{q}',t)$ obeys the equation:

$$\begin{gathered}\left(\frac{\partial}{\partial t} - \hat{\mathscr{T}}(\vec{q}) - i\hat{\hat{L}}(\vec{q})\right)\hat{\hat{\varphi}}(\vec{q},\vec{q}',t) = \delta(\vec{q}-\vec{q}')\,\delta(t) \\ \hat{\hat{\varphi}}(\vec{q},\vec{q}',0) = \delta(\vec{q}-\vec{q}'),\quad \vec{q} \neq \vec{q}'\end{gathered} \tag{4}$$

Here the operator $\hat{\mathscr{T}}(\vec{q})$ describes the relative motion of radicals in the configuration space, which is assumed to be independent of the spin state of the radicals; $\hat{\hat{L}}(\vec{q}) = \hat{\hat{L}} - \hat{\hat{J}}(\vec{q})$ is the Liouvillian, which describes the coordinate-independent spin evolution determined by the Zeeman and HFI interactions ($\hat{\hat{L}}$) and the evolution determined by the exchange interaction ($\hat{\hat{J}}(\vec{q})$). It is assumed that in nonviscous solutions the main contribution to the spin evolution is made by the coordinate-independent term of the Liouvillian $\hat{\hat{L}}$.[1] The S−T$_-$ (or S−T$_0$) transitions in the region of energy levels crossing are not taken into consideration.

The direct calculations of the matrix elements of matrix $\vec{q}$, particularly, for weak magnetic fields, by eq 4 are fairly elaborate. Therefore, to derive analytical formulas, we shall make some simplifying assumptions. First, it is clear that, most generally, the zones of the singlet and triplet energy levels crossing are rather narrow (regions of the configuration space). Thus, transitions that occur in these zones can be taken into account in the balance approximation.[22,23] Let us represent the Liouville matrix $i\hat{\hat{L}}(\vec{q})$) as

$$i\hat{\hat{L}}(\vec{q}) = i\hat{\hat{L}} - \hat{\hat{V}}(\vec{q}) \tag{5}$$

Operator $\hat{\hat{V}}(\vec{q})$ describes the S−T$_-$ transitions that occur in the region of energy levels crossing in the balance approximation. We assume[23] that

$$\hat{\hat{V}}(\vec{q}) = \hat{\hat{V}}_0\delta(E_s(\vec{q}) - E_{T\_}(\vec{q})) \tag{6}$$

where $E_s(\vec{q})$ and $E_{T-}(\vec{q})$ are the $\vec{q}$ dependencies of the energy levels of the S and T$_-$ terms, respectively.

To find the $\hat{\hat{g}}$ matrix, we introduce the Laplace transform of the $\hat{\hat{\varphi}}(\vec{q},\vec{q}',t)$ matrix, $\hat{\hat{G}}(\vec{q},\vec{q}',s)$. It can be readily seen from eqs 4 and 6 that the operator obeys the equation

$$(\hat{\mathscr{T}}(\vec{q}) + i\hat{\hat{L}} - \hat{\hat{V}}(\vec{q}) - s)\hat{\hat{G}}(\vec{q},\vec{q}',s) = -\delta(\vec{q}-\vec{q}') \tag{7}$$

Thus the $\hat{\hat{g}}$ matrix is expressed in terms of $\hat{\hat{G}}(\vec{q},\vec{q}',s)$ as follows:

$$\hat{\hat{g}} = \int\!\!\int \psi(\vec{q})\, \hat{\hat{G}}(\vec{q},\vec{q}',0)\, \psi(\vec{q}')\, \mathrm{d}\vec{q}\, \mathrm{d}\vec{q}' \tag{8}$$

Equation 7 is rearranged to the integral equation

$$\begin{aligned}\hat{\hat{G}}(\vec{q},\vec{q}',s) = \hat{\hat{G}}_0(\vec{q},\vec{q}',s) - \\ \int \hat{\hat{G}}_0(\vec{q},\vec{q}'',s)\, \hat{\hat{V}}(\vec{q}'')\, \hat{\hat{G}}(\vec{q}'',\vec{q}',s)\, \mathrm{d}\vec{q}''\end{aligned} \tag{9}$$

where

$$\begin{aligned}\hat{\hat{G}}_0(\vec{q},\vec{q}',s) = \int_0^\infty \varphi(\vec{q},\vec{q}',t)\, \exp(i\hat{\hat{L}}t - st)\, \mathrm{d}t \equiv \\ \int_0^\infty \varphi(\vec{q},\vec{q}',t)\, \hat{\hat{T}}(t)\, \exp(-st)\, \mathrm{d}t\end{aligned} \tag{10}$$

The function $\varphi(\vec{q},\vec{q}',t)$ is the conditional probability density of the realization of coordinate $\vec{q}$, which initially was equal to $\vec{q}'$ at time t. This function completely defines the kinematics of the relative motion of partners and obeys the equation

$$\begin{gathered}\left(\frac{\partial}{\partial t} - \hat{\mathscr{T}}(\vec{q})\right)\varphi(\vec{q},\vec{q}',t) = \delta(\vec{q}-\vec{q}')\,\delta(t) \\ \varphi(\vec{q},\vec{q}',0) = \delta(\vec{q}-\vec{q}'),\quad \vec{q} \neq \vec{q}'\end{gathered} \tag{11}$$

Generally speaking, eq 9 can be represented as an algebraic system of equations and thus readily solved. However, since the dimensionality of this system is large, its analytical solutions is cumbersome. Therefore, for simplification we assume that the RP's lifetime in cage is too short for the singlet—triplet transitions to significantly affect the populations of electron—nuclear spin states. Thus, it is assumed that the efficiency of the singlet—triplet transitions is not very high. Then, eq 9 is solved by the method of successive approximations. In the first approximation, we have

$$\hat{\hat{G}}(\vec{q},\vec{q}',s) = \hat{\hat{G}}_0(\vec{q},\vec{q}',s) - \int \hat{\hat{G}}_0(\vec{q},\vec{q}'',s)\, \hat{\hat{V}}(\vec{q}'')\, \hat{\hat{G}}_0(\vec{q}'',\vec{q}',s) \tag{12}$$

The $\hat{\hat{G}}_0(\vec{q},\vec{q}',s)$ matrix is expressed in terms of the $\hat{\hat{T}}(t)$ matrix by formula 10. For RP with one magnetic nucleus with the spin $I = {}^1/_2$, the $\hat{\hat{T}}(t)$ matrix is also available.[24] Thus, to find $\hat{\hat{G}}(\vec{q},\vec{q}',s)$, it suffices to determine the matrix elements of the $\hat{\hat{V}}(\vec{q})$ matrix. For the RP subensemble with $m = +{}^1/_2$ in the singlet state, where singlet and triplet terms do not interact, all elements of $\hat{\hat{V}}(\vec{q})$ are zero. For the subensemble with $m = -{}^1/_2$, four matrix elements differ from zero:

$$(\hat{\hat{V}}(\vec{q}))_{SS,SS} = (\hat{\hat{V}}(\vec{q}))_{T\_T\_,T\_T\_} = -(\hat{\hat{V}}(\vec{q}))_{SS,T\_T\_} = -(\hat{\hat{V}}(\vec{q}))_{T\_T\_,SS} \equiv V(\vec{q}) \quad (13)$$

To calculate τ_m one needs only four elements of the $\hat{T}(t)$ matrix:

$$\begin{aligned}(\hat{\hat{T}}(t))_{SS,SS} &= (1 - F_{12} - F_{13})\\ (\hat{\hat{T}}(t))_{SS,T\_T\_} &= (\hat{\hat{T}}(t))_{T\_T\_,SS} = F_{13}\\ (\hat{\hat{T}}(t))_{T\_T\_,T\_T\_} &= (1 - 2F_{13})\end{aligned} \quad (14)$$

where[25]

$$F_{12} = (-\cos^2\varphi \sin^2\varphi(1 - \cos(E_1 - E_3)t) + \cos^2\varphi(1 - \cos(E_1 - E_2)t) + \sin^2\varphi(1 - \cos(E_2 - E_3)t))/2 \quad (15)$$

$$F_{13} = \cos^2\varphi \sin^2\varphi(1 - \cos(E_1 - E_3)t)$$

Here E_1, E_2, and E_3 are the steady state energy levels

$$\begin{aligned}E_1 &= -(\omega_2 + a/2 - \sqrt{\omega_1^2 + a^2})/2\\ E_2 &= -(\omega_1 - \omega_2 - a/2)/2\\ E_3 &= -(\omega_2 + a/2 + \sqrt{\omega_1^2 + a^2})/2\end{aligned} \quad (16)$$

For brevity, we use the designation

$$\cos^2\varphi = \frac{1}{2}\left(1 + \frac{\omega_1}{\sqrt{\omega_1^2 + a^2}}\right) \quad (17)$$

In formulas 16 and 17, ω_1 and ω_2 denote the Zeeman precession frequencies of the unpaired electrons of the pair of radicals, and a denotes the HFI constant in frequency units.

For simplicity, we assume that the matrix element of transition $\hat{V}(\vec{q})$ depends only on the distance between the unpaired electrons of radicals, and the exchange interaction decreases with distance exponentially. Then,

$$V(\vec{q}) \equiv V(r) = K_c\delta(r - r_c) \quad (18)$$

For K_c, we one can use the familiar expression[3,5]

$$K_c = \pi^2 r_c^2 \frac{a^2\lambda}{E} \quad (19)$$

Here λ is the characteristic scale of the exchange interaction decay; $E = (\omega_1 + \omega_2)/2 + a/4$; r_c is the distance at which the singlet and triplet terms intersect, $r_c = R + \lambda \ln(2J_0/E)$. Now, substituting eqs 18 and 14 into eq 3, we get the following expression for τ_m:

$$\tau_m = g(R,R,0) - b(R,R) - c(R,R) - \frac{K_c}{v}(2g(r_c,R,0) - b(r_c,R) - 5c(r_c,R))(g(r_c,R,0) - b(r_c,R) - 2c(r_c,R)) \quad (20)$$

where v is the reaction zone volume. We use the designations

$$b(r,R) = \frac{1}{2}\{(1 - \cos^2\varphi \sin^2\varphi)g(r,R,0) + \cos^2\varphi \sin^2\varphi\, Re(g(r,R,i(E_1 - E_3))) - \cos^2\varphi\, Re(g(r,R,i(E_1 - E_2))) - \sin^2\varphi\, Re(g(r,R,i(E_2 - E_3)))\} \quad (21)$$

$$c(r,R) = \cos^2\varphi \sin^2\varphi(g(r,R,0) - Re(g(r,R,i(E_1 - E_3))))$$

Thus, the time τ_m is expressed in terms of the universal function $g(r,R,s)$, which defines the kinematics of the relative motion of radicals in the pair; $g(r,R,s)$ is related to the conditional probability density $\varphi(r,R,t)$ as follows:

$$g(r,R,s) = \int_0^\infty \varphi(r,R,t)\exp(-st)\,dt \quad (22)$$

For the relative diffusion motion of radicals with the diffusion coefficient D, the function $g(r,R,s)$ takes the form

$$g(r,R,s) = \frac{\tau_p R}{r}\frac{\exp(-(r - R)\sqrt{s/D})}{1 + \sqrt{sR^2/D}} \quad (23)$$

where $\tau_p = R\delta/D$ is the residence time in the reaction zone. For simplicity in our calculations, the size of reaction zone is equal to the characteristic scale of exchange interaction decay ($\lambda = \delta$).

The approach based on the Green function formalism allows the consideration of a more general case, where the reactivity anisotropy and the exchange interaction anisotropy are taken into account. The reactivity anisotropy is defined by the steric factor f and, naturally, should be averaged by translational and rotational motions of radicals. In the simplest case, the effective shape of the zone of energy levels crossing is also be defined by a steric factor f_1, and for estimation, it can be assumed that $f_1 \approx f$. We calculated the CIDNP taking into account the anisotropic character of the reactivity and exchange interaction. No qualitative changes in the field dependencies were found. However, it should be noted that the scale of the effect varies significantly with the parameters J_0, λ, D, f_1, and f.

Discussion

The ratio between polarization formed due to the $S-T_0$ and $S-T_-$ transitions (terms of eq 5) determines the shape of the CIDNP magnetic field dependence and the polarization sign. With the $S-T_0$ channel prevailing, which is characteristic of the systems with rather small HFI constants in homogeneous solutions, the CIDNP magnetic field dependence is of typical form with a maximum in the region of the HFI constant (Figure 4a, upper curve), and the polarization sign is determined by the Kaptein rule for weak fields.[1,25] The $S-T_0$ mechanism determined by the transitions independent of the exchange interaction leads to the formation of the effective CIDNP if the lifetime $\tau_c = R^2/D$ in the cage is less than the characteristic time of the $S-T_0$ transitions $\sim(a/2)^{-1}$, i.e., $a\tau_c/2 < 1$, which provides a competition between the singlet−triplet conversion of RPs with the α- and β-orientations of nuclear spins. If the parameter $a\tau_c/2$ exceeds unity (the cases of large HFI constants or long RP's lifetime), spin evolution becomes essentially averaged, and the efficiency of CIDNP formation by this mechanism decreases. On the contrary, the CIDNP intensity determined by $S-T_-$ transitions in the region of energy levels crossing is proportional to a^2. Therefore, the HFI constant increase leads to the increase in the contribution of $S-T_-$ mechanism into CIDNP formation.

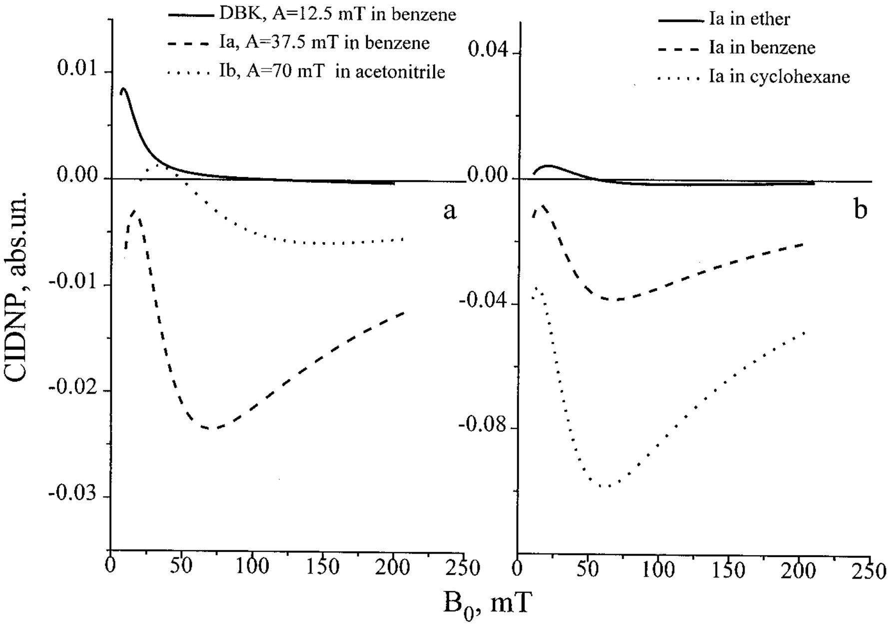


Figure 4. The influence of the various parameters on CIDNP field dependencies calculated by eq 1. (a) Variation of HFI constant; other parameters: $J_0 = -1.8 \times 10^{17}$ rad/s, $\lambda = 0.4$ Å, $R = 6$ Å for DBK, BDMP and $R = 7$ Å for TMBDPO; g_1 and g_2 for TMBDPO, BDMP, and DBK see Figures 2, 3, and 4, respectively. (b) Variation of the solvent ($A = 37.5$ mT, $\lambda = 0.4$ Å, $R = 7$ Å).

The sizes of diphenylphosphonyl and dimethoxyphosphonyl radicals differ only slightly from the sizes of phenacyl or benzoyl radicals. It seems likely that the reactivities of these radicals also differ insignificantly. In fact, the only difference is the value of HFI constant: 12.3−12.5 mT (carbonyl ^{13}C nuclei) for acyl radicals and 37−70 mT (^{31}P nuclei) for phosphonyl radicals. For benzoyl radical ($A = 12.5$ mT, $R = 6$ Å) in ether ($\eta = 0.233$ cP), $a\tau_c/2 \approx 0.3$, while for phosphonyl radical ($A = 40$ mT, $R = 7$ Å), $a\tau_c/2 \approx 0.9$. Thus, for HFI constants >40 mT, the intensity of the CIDNP formed due to $S-T_0$ transitions decreases, while the intensity of the CIDNP results from the $S-T_-$ transitions increases. Thus, we believe that changes in the signs and shapes of the experimental CIDNP field dependencies with increasing of HFI constant show that the role of $S-T_-$ transitions are growing in importance for the formation of CIDNP.

Figure 4a shows the CIDNP field dependence calculated by formula 20 with different values of HFI constants. As one might expect, at relatively small HFI constants ($A = 12.5$ mT) the main contribution to the polarization is made by the singlet−triplet transitions independent of the exchange interaction. The polarization is formed at the interradical distances such that the exchange interaction is nearly zero. It can be seen that the model is rather adequate to explain experimental results for systems with small HFI constants. At $A = (h/g\beta)a \approx 38$ mT (diphenylphosphonyl radical) and higher 70 mT (dimethoxyphosphonyl radical) (at constant J_0 and λ), the main contribution to the polarization is made by the singlet−triplet transitions that proceed in the region of energy level crossing. As a result, the CIDNP effect changes its sign (Figure 4a).

Another important parameter that governs the ratio between $S-T_0$ and $S-T_-$ transitions is the diffusion coefficient of the solvent D. The latter determined the residence time in the region of $S-T_-$ energy levels crossing $\tau_p = R\lambda/D$ as well as the lifetime in the solvent cage $\tau_c = R^2/D$. Going from the ether to ethanol ($\eta = 1.2$ cP) and then to micellar solutions ($\eta \approx 20$ cP) is accompanied by an increase in the τ_c and thus by a decrease in the $S-T_0$ contribution to polarization. The efficiency of the $S-T_-$ transitions and their contribution to the CIDNP increase as the decreasing of D leads to the increasing of the residence time in the region where $S-T_-$ energy levels crossing. Figure 4b shows the field dependencies for TMBDPO in several solvents calculated by eq 20. It can be seen that the calculated curves are in qualitative agreement with the experimental results; however, in the case of nonviscous solvents, the model considerably overestimates the contribution of the $S-T_0$ transitions.

Comparison between the experimental and calculated CIDNP field dependencies presents some other difficulties. Among them are different radical reactivities in different solvents and the solvation conditions. It is obvious that the rates of recombination from the singlet state (U_0 in eq 2) differ in different solvents, which leads to variations in the ration of CIDNP intensities in solvents with similar viscosities. According to our estimations, in photolysis of TMBDPO in benzene, the CIDNP intensity is approximately 5 times lower than that in acetonitrile, although benzene is a more viscous solvent (cf. Figure 4b). Formation of hydrogen bonds with both the original molecule and arising radicals can change the U_0 in ethanol. However, it seems likely that, despite their influence on U_0, i.e., on the absolute value of polarization (see eq 2), the above factors do not considerably affect the shapes of the curves.

A disadvantage of this model is the application of the balance approximation to the description of the $S-T_-$ transitions, which results in the dependence of J_0 on the range of magnetic fields under study (eq 19). At very weak magnetic fields ($\omega < a$), the region of energy levels crossing is significantly broadened, and the balance approximation can correctly predict only the qualitative behavior of the CIDNP. In addition, at small solvent viscosities, the model is highly sensitive to the magnitude of the effective exchange interaction, which is defined by parameters R and λ (parts a and b of Figure 5). The higher R and λ, the higher the efficiency of the $S-T_-$ transitions and of the corresponding polarization.

The results obtained by the numerical solution of the stochastic Liouville equation in the microreactor model[26] and by using the finite-difference scheme of Pedersen and Freed[27] are more consistent with the experimental data. To model a homogeneous solution as described elsewhere,[20] we used the microreactor radius 400 Å and the scavenging rate constant $k_{scv} = 5 \times 10^6$ s^{-1}. These values obey the condition $1/k_{scv} < Z^{-1} < \tau_d$, where Z is the characteristic time between collisions, Z^{-1}

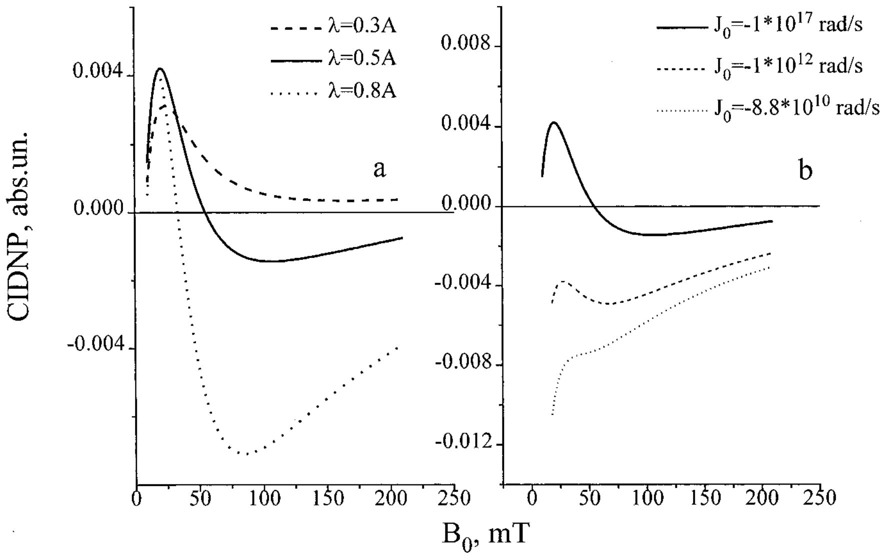


Figure 5. The CIDNP field dependencies calculated by eq 1: (a) variation of λ (A = 37.5 mT, R = 7 Å, in ether); (b) variation of J_0 (A = 37.5 mT, λ = 0.4 Å, R = 7 Å, in ether).

$= L^3/3RD$, and τ_d is the mean RP lifetime in the microreactor, $\tau_d = L^2/D$. The exchange interaction was assumed to decay exponentially with λ. The microreactor radius was divided into 5000 shells. Relaxation of radicals in the pair was neglected. Recombination of RP in the reaction zone of thickness $\delta = \lambda$ was described by the dimensionless value $k_s\tau$, where k_s is the rate constant of recombination from the singlet state within the reaction zone, $\tau = R\delta/D$ is the rate RP residence time within the reaction zone, D is the mutual diffusion coefficient, and R is the reaction radius. Figure 2b shows the calculation results for the photolysis of **Ia** in the solvents used in experiments. It is seen that, in the case of the diffusion-controlled reaction ($k_s\tau \approx 7-10$, i.e., recombination probability $k_s\tau/(1 + k_s\tau) \rightarrow 1$), the numerical solution is adequate to reproduce the viscosity dependence of the experimental curves. However, in this case, in order to obtain the emission CIDNP field dependence, one should employ much greater values of J_0 as compared to those optimized in the simulation of the SNP spectra for the same RP in micellar solutions.[13] At $k_s\tau < 5$, the maxima of the calculated field dependencies are extremely sensitive to the solvent. The numerical calculation (Figure 3) is also adequate to represent the field dependence of the CIDNP obtained in the photolysis of **Ib** in acetonitrile. It should be noted, however, that certain differences between the models for calculating the field dependencies make it impossible to compare the values of J_0 obtained in analytical and numerical calculations.

Another peculiarity which should be taken into consideration when simulating field dependencies is taking account of electron polarization formed due to triplet mechanism.[1] The short lifetime of a triplet molecule preceding RP formation results in the transfer of nonequilibrium population of T_x,T_y,T_z levels to T_+,T_-,T_0 levels of a radical pair. For TMBDPO the parameters of triplet molecule in toluene/ethanol glass at 20 K were obtained in ref 7. On the other hand, it is known that the lifetime of triplet TMBDPO molecule in benzene is about 0.3 ns at room temperature,[8] and the CIDEP by triplet mechanism observed in TR ESR spectra in homogeneous and micelle solutions is essential.[13-15] Thus one can expect greater initial population of T_- level in the RP being formed which is to enhance emission in the field dependence. Moreover, the value of the transferred polarization decreases with the increasing rate of reorientation relaxation of molecules;[1] thus the contribution of triplet polarization into the observed CIDNP will be most significant in ethanol, gradually decreasing to ether. Numerical calculations for ethanol have shown that taking account of triplet polarization contribution using the parameters published in ref 7 makes it possible to reduce essentially the exchange interaction value $|J_0|$ from 4.4 × 10^{10} to 3.5 × 10^{10} rad/s, thus making it closer to the value obtained in SNP spectra calculations in micelle solutions. However, in other solvents, it fails to reconstruct experimental results adequately.

Conclusion

Field dependencies of CIDNP obtained in TMBDPO and BDMP photolysis in homogeneous solutions points to a considerable contribution of $S-T_-$ transitions proceeding in the terms interaction zone into the observed CIDNP effect. The efficiency of such transitions increases with the solvent viscosity, which is due to the increase in RP residence time in the region where $S-T_-$ energy levels cross.

The analytical formula for the calculation of CIDNP field dependencies is proposed. It is based on a theoretical model which makes it possible to allow for $S-T_-$ transitions dependent on the exchange interaction, in the balance approximation. Qualitative agreement between the results calculated by this model and experimental evidence is observed. However, the model has some drawbacks determined by the approximations employed, such as noticeable broadening of the terms interaction zone in very weak magnetic fields, bound on the value J_0 and overestimation of the role of $S-T_0$ transitions at short distances between the radicals.

Comparison is made between experimental findings and the results of the calculations by the method of numerical solution of the Liouville equation for a microreactor model. The rather good agreement between calculated and experimental field dependencies has been obtained. However, better agreement calls for taking account of such factors as variation of the reactivity of radicals in different solutions and, as for example in the case of TMBDPO, consideration of triplet polarization contribution into CIDNP effect.

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