Low Magnetic Field Dependence of the ^{31}P Chemically Induced Dynamic Nuclear Polarization in the Photolysis of a Benzoyl Phosphonate. Role of S−T$_-$ Mechanism

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The chemically induced dynamic nuclear polarization (CIDNP) upon the photolysis of 2,4,6-trimethylbenzoylphosphonic acid dimethyl ester in solvents of different viscosities has been studied in high and low magnetic fields. The reaction was carried out in the presence of an effective radical scavenger, bromotrichloromethane, which allows the study of only the geminate contribution to the CIDNP. The theory proposed earlier, considering S−T$_-$ transitions in the level crossing region in the balance approximation, has been modified by taking into account the reaction with scavengers, anisotropy of the exchange interaction, and the reactivity of radicals and has been used for the description of the CIDNP field dependencies obtained. Good agreement of theoretical and experimental results is achieved with the following set of parameters: $J_0 = -450 \pm 100$ mT, $\lambda = 0.7 \pm 0.1$ Å, f (steric factor) $= 0.08 \pm 0.02$, τ_r (correlation time of modulation of the exchange interaction and reactivity anisotropy) $= 7 \pm 2$ ps (in CH$_3$CN), 25 ± 3 ps (in dioxane).

Introduction

It is known[1] that the magnetic and spins effects in reactions of radical pairs (RPs) with large HFI constants in low magnetic fields have a number of features caused by S−T$_-$ transitions occurring in the region of the S−T$_-$ level crossing. The influence of S−T$_-$ transitions on chemically induced dynamic nuclear polarization (CIDNP) and chemically induced dynamic electron polarization (CIDEP) effects for RP with a large HFI constant in homogeneous solutions was earlier investigated in a number of studies.[2−8] Recently,[7] we carried out an experimental and theoretical investigation of the CIDNP field dependencies for RP with a large HFI constant, formed during the photolysis of (2,4,6-trimethybenzoyl)diphenylphosphine oxide (TMDPO) and benzoylphosphonic acid dimethyl ester in organic solvents of different viscosity. For the description of experimental data, an analytical formula has been proposed based on a theoretical model taking into account S−T$_-$ transitions in the balance approximation. Qualitative agreement between theory and experimental results was observed, but quantitative agreement was not achieved. Some reasons for such disagreement may be the following. First, CIDNP, which can be transferred from the strong electron polarization formed as a result of the triplet mechanism upon the photolysis of TMDPO, was not taken into account in the calculations. Second, the CIDNP contribution of only in-cage products was taken into account despite the fact that the CIDNP is formed by both in-cage and escape products. It was assumed that the CIDNP contribution of the escaped product is not substantial. But such an assumption is correct only when the CIDNP of in-cage and escaped products are equal in magnitude and opposite in sign, i.e., when the contribution of S−T$_-$ transitions can be neglected. However, CIDNP due to S−T$_-$ transitions occurring in a level crossing region is identical in sign for in-cage and for escaped

products. Therefore, CIDNP observed in products formed both as in-cage and escaped can be determined by S−T$_-$ transitions occurring in a level crossing zone, even when this contribution is significantly less than CIDNP from S−T$_0$, S−T$_+$, and S−T$_-$ transitions occurring in a zone with zero exchange interaction.

In this work we report the results of a low magnetic field CIDNP study for RPs with large HFI constants. To distinguish the CIDNP contribution of geminate RPs, we have used scavenging of escape radicals, which has allowed us to carry out a quantitative comparison of experimental and calculated data. Also, the theoretical model has been developed to take into account the reaction with scavengers and the influence of anisotropy of exchange interaction as well as reactivity of radicals on CIDNP field dependencies.

Results

We investigated the CIDNP field dependencies in the photolysis of 2,4,6-trimethylbenzoylphosphonic acid dimethyl ester (**I**) in acetonitrile and dioxane in the absence and presence of a radical scavenger (bromotrichloromethane). The main radical reactions with **I** are presented in the Schemes 1 and 2.[9−11] The photolysis of **I** in a number organic solvents leads to C(O)−P bond cleavage from a singlet as well as from a triplet state[9] and the formation of trimethylbenzoyl and dimethoxyphosphonyl radicals, and also to a nonradical route of the reaction.[9] The intermediate RP has nonzero HFI constants only for the dimethoxyphosphonyl radical $A(^{31}$P$) = 69.6-70$ mT and $A(^1$H$) = 6 \times 0.06$ mT in two methoxy groups.[6] According to ref 11, the contribution of the singlet precursor to the observed CIDNP can be neglected.

Figure 1 shows the ^{31}P CIDNP spectrum detected upon the photolysis of **I** in acetonitrile at 42 mT in the absence (a) and presence (b) of CBrCl$_3$. The peaks were assigned using literature data for a similar compound.[10] CIDNP of all products is emissive in the absence of scavenger despite the rules for low magnetic fields,[12] which predict absorption for **I** (in-cage product of RP with positive HFI). The addition of CBrCl$_3$ changes the sign of

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SCHEME 1
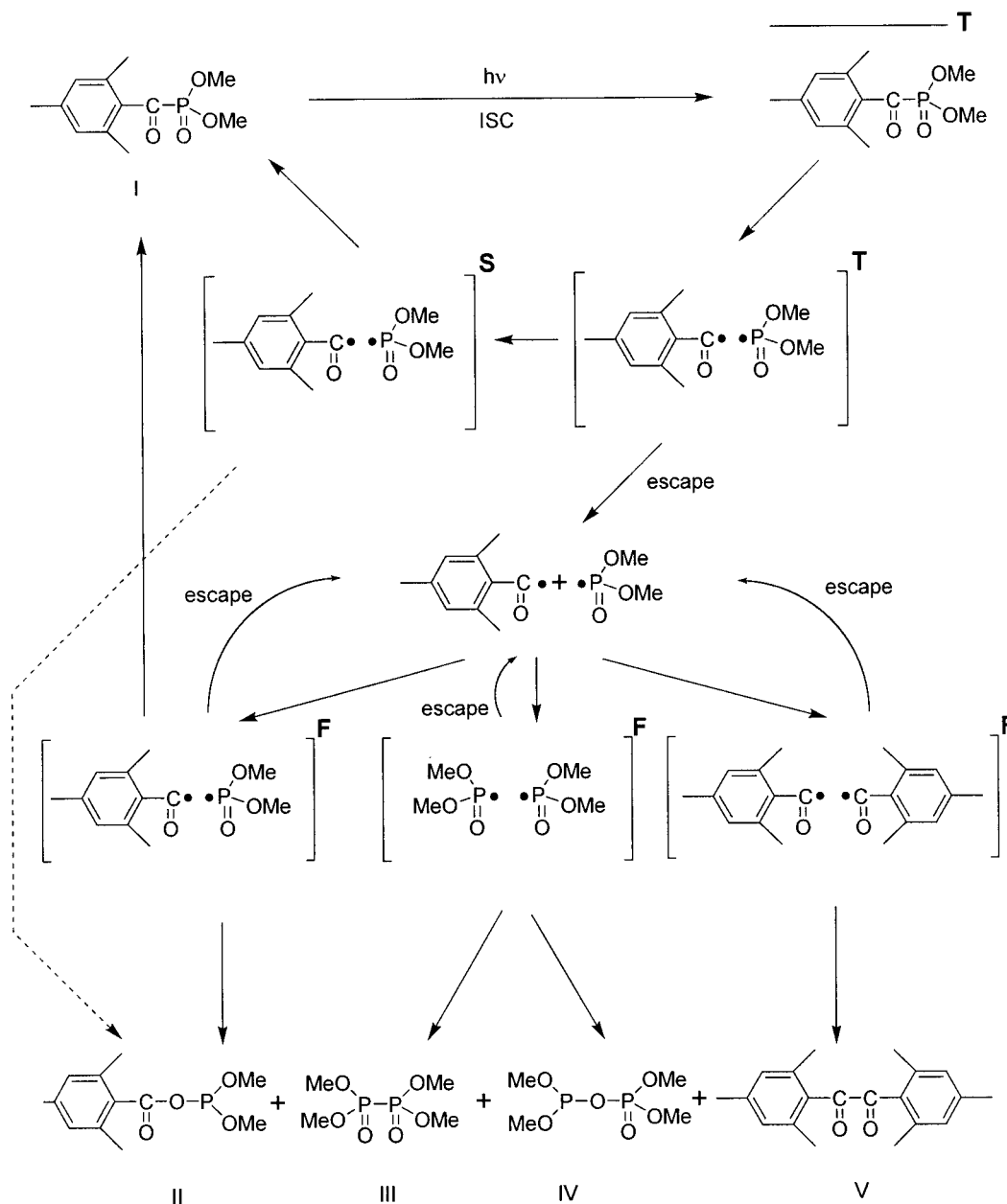
CIDNP of **I** from emission to absorption. The CIDNP of the dimethylphosphorobromidate (**VI**) (-4 ppm) is observed with very low signal-to-noise ratio at about 70 mT. The low intensity of CIDNP can be explained by the loss of CIDNP during the transport of the sample from the photochemical cell to the NMR probe due to the short nuclear relaxation time of the ^{31}P nuclei in **VI**. In addition, there is no CIDNP for the (2,4,6-trimethylbenzoyl)dimethyl phosphite (**II**) in the presence of scavenger.

Figure 2 presents the CIDNP field dependencies obtained in the photolysis of **I** in acetonitrile and dioxane, detected by ^{31}P NMR signals of **I**, both in the absence (a) and in the presence (b) of the scavenger. All curves are obtained at the same light intensity and flow rate. One can see that the addition of CBrCl$_3$ results in a change of CIDNP sign from emission to absorption.

The same polarized products of the photolysis of **I** are observed in the ^{31}P NMR spectrum at high magnetic field, $B_0 = 2.1$ T (Figure 1c). The signs of CIDNP of **I** and **II** are absorptive in both solvents and are in good agreement with the Kaptein rules.[13]

Tetramethylhypophosphate (**III**) and tetramethylsubphosphate (**IV**) are formed only in diffusional radical pairs (F-pairs). CIDNP of these compounds is emissive at low magnetic fields and can be observed only at concentrations of CBrCl$_3$ lower than 0.117 M. In addition, compound **IV** shows an E/A multiplet polarization (A is absorption and E is emission) (Figure 1, inset). That corresponds to a negative ^{31}P$-^{31}$P coupling constant[14] in this compound ($^2J_{\text{P}-\text{P}} = -7$ Hz). At $B_0 = 2.1$ T a net CIDNP is observed only for compound **III** and only in acetonitrile (absorption). In dioxane the signal from this compound is absent. E/A multiplet polarization for compound **IV** has been detected.

Theory

The theory of CIDNP, taking account of the S$-$T$_-$ transitions in the balance approximation, has been described in ref 7 in detail. Below we shall briefly consider the changes that are made in the final equation by taking into account the reaction of radicals with a scavenger, the anisotropy of the exchange interaction, and the reactivity of radicals.
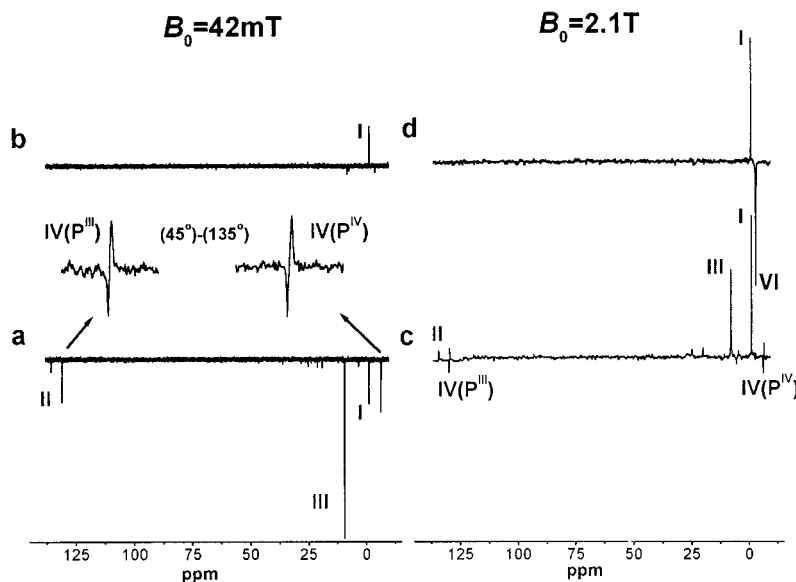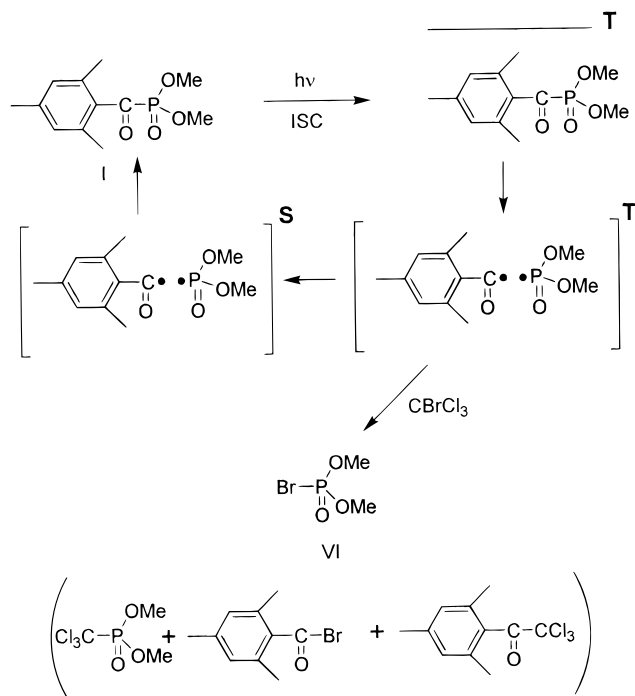
Figure 1. CIDNP ^{31}P spectra upon the photolysis of **I** in CH$_3$CN in the absence (a, c) and in the presence (b, d) of CBrCl$_3$ at low and high magnetic fields. Inset: multiplet CIDNP on NMR signals of **IV** obtained by subtraction of spectra recorded using 45° and 135° rf pulses.

SCHEME 2

Reaction of Radicals with a Scavenger. The CIDNP is characterized by the average value of the operator $\hat{I}_{kz}$ of the nuclear spin in recombination products:[1]

$$\langle \hat{I}_{kz} \rangle = \mathrm{Tr}_{A,B}\{\hat{I}_{kz}\hat{w}\} \tag{1}$$

where $\mathrm{Tr}_{A,B}$ is the trace of the operator on all spin states of radicals A and B, and $\hat{w}$ is recombination probability of RP subensembles with different orientations of the nuclear spins. The matrix $\hat{w}$ is expressed through a matrix $\hat{\hat{g}}$ that specifies both the kinematics of the relative motion of radicals in the configuration space and the spin evolution of the pair:[15]

$$\hat{w} = \hat{\hat{K}}_r\hat{\hat{g}}(1 + \hat{\hat{K}}_r\hat{\hat{g}})^{-1}\rho_0 \tag{2}$$

$\hat{\hat{K}}_r$ is the Liouville matrix of recombination constants from one
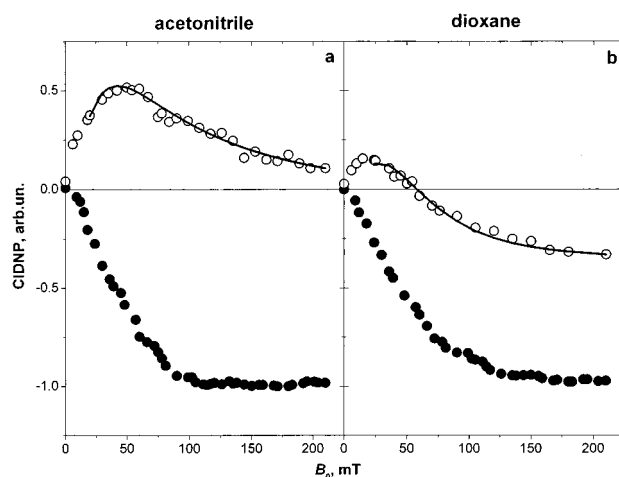

Figure 2. CIDNP ^{31}P field dependencies upon the photolysis of **I** in the absence (●) and in the presence (○) of CBrCl$_3$ at low magnetic fields. Solid lines are calculated using eqs 1, 2, and 16 with the following set of parameters: $J_0 = -450 \pm 100$ mT, $\lambda = 0.7 \pm 0.1$ Å, $f = 0.08 \pm 0.02$, $\tau_r = 7 \pm 2$ ps (in CH$_3$CN), 25 ± 3 ps (in dioxane).

or another spin state, ρ_0 is the density matrix of RP at $t = 0$, and

$$\hat{\hat{g}} = \lim_{s\to 0}\frac{1}{v}\int_v\int_v\hat{\hat{G}}(\vec{q},\vec{q}';s)\,\mathrm{d}\vec{q}\,\mathrm{d}\vec{q}' \tag{3}$$

The function $\hat{\hat{G}}(\vec{q},\vec{q}';s)$ obeys the equation

$$(\hat{\mathcal{F}}(\vec{q}) + i\hat{\hat{L}}(\vec{q}) - s)\hat{\hat{G}}(\vec{q},\vec{q}';s) = -\delta(\vec{q} - \vec{q}') \tag{4}$$

Here, the operator $\hat{\mathcal{F}}(\vec{q})$ describes the relative motion of radicals in the configuration space, which is assumed to be independent of the spin state of the radicals.

In the balance approximation the matrix $\hat{\hat{G}}(\vec{q},\vec{q}';s)$ can be written for low viscous solutions as[7]

$$\hat{\hat{G}}(\vec{q},\vec{q}';s) = \hat{\hat{G}}_0(\vec{q},\vec{q}';s) -$$
$$\int \hat{\hat{G}}_0(\vec{q},\vec{q}'';s)\hat{\hat{V}}(\vec{q}'')\hat{\hat{G}}_0(\vec{q}'',\vec{q}';s)\,\mathrm{d}\vec{q}'' \tag{5}$$

The operator $\hat{\hat{V}}(\vec{q})$ describes S−T$_-$ transitions occurring in a level crossing zone, in the balance approximation. For the

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simplest case $\hat{V}(\vec{q}) = \hat{V}_0 \delta(E_S(\vec{q}) - E_{T_-}(\vec{q}))$. The matrix $\hat{G}(\vec{q},\vec{q}';s)$ is expressed in terms of the operator of spin evolution $\hat{T}_0(t)$:

$$\hat{G}_0(\vec{q},\vec{q}';s) = \int_0^\infty \hat{T}_0(t) \exp(-(s + K_s)t) \varphi(\vec{q},\vec{q}';t)\, dt \quad (6)$$

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:

$$\left(\frac{\partial}{\partial t} - \hat{\mathcal{F}}(\vec{q})\right)\varphi(\vec{q},\vec{q}';t) = \delta(\vec{q} - \vec{q}')\delta(t)$$

For RP with one magnetic nucleus with spin $I = {}^1/_2$ the $\hat{T}(t)$ matrix is known.[16] For the subensemble of RPs with $m = -{}^1/_2$, in the basis $|SS\rangle$, $|T_0T_0\rangle$, $|T_-T_-\rangle$ this matrix is

$$\hat{T}_0(t) = \begin{bmatrix} 1 - F_{12} - F_{13} & F_{12} & F_{13} \\ F_{12} & 1 - F_{12} - F_{13} & F_{13} \\ F_{13} & F_{13} & 1 - 2F_{13} \end{bmatrix} \quad (7)$$

where

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

$$F_{13} = \cos^2\varphi \sin^2\varphi(1 - \cos(E_1 - E_3)t) \quad (8)$$

where

$$E_1 = -(\omega_2 + a/2 - \sqrt{\omega_1^2 + a^2})/2$$

$$E_2 = -(\omega_1 - \omega_2 - a/2)/2$$

$$E_3 = -(\omega_2 + a/2 + \sqrt{\omega_1^2 + a^2})/2 \quad (9)$$

$$\cos^2\varphi = \frac{1}{2}\left(1 + \frac{\omega_1}{\sqrt{\omega_1^2 + a^2}}\right) \quad (10)$$

For relative diffusional motion of spherical radicals, with isotropic reactivity and exchange interaction, the function $g(r,R,s)$ is the following:[17]

$$g(r,R,s) = \int_0^\infty \varphi(r,R,t) \exp(-st)\, dt =$$
$$\frac{\tau_p R}{r} \frac{\exp(-(r - R)\sqrt{s/D})}{1 + \sqrt{sR^2/D}} \quad (11)$$

where $\tau_p = R\Delta/D$ and D is the diffusion coefficient. It is easy to see that the matrix elements of the matrix $\hat{g}$ are expressed through functions of eq 11. The matrix elements of the operator $\hat{V}(\vec{q})$ are equal:

$$(\hat{V}(\vec{q}))_{SS,SS} = (\hat{V}(\vec{q}))_{T_-T_-,T_-T_-} = -(\hat{V}(\vec{q}))_{SS,T_-T_-} =$$
$$-(\hat{V}(\vec{q}))_{T_-T_-,SS} = \pi r_c \frac{2a^2\lambda}{E} \quad (12)$$

where $r_c = R + \lambda \ln(2J_0/E)$, λ is the characteristic scale of decay of the exchange interaction, $E = (\omega_1 + \omega_2)/2 + a/4$, ω_1 and ω_2 denote the Zeeman precession frequencies of the unpaired electrons, and R is the sum of the radii of the radicals of the pair. For simplicity in our calculations, the size of the reaction zone is taken to be equal to the characteristic scale of decay of the exchange interaction: $\lambda = \Delta$.

For the reaction under study, RP is formed in the triplet state and recombines in the singlet state; i.e., $\rho_0 = (0; 1/3; 1/3)$, $(\hat{K}_r)_{SS,SS} = K_r$, $(\hat{K}_r)_{TT,TT} = 0$ (T = T$_0$, T$_+$, T$_-$).

The main assumption of the balance approximation is that the S$-$T$_-$ transitions take place only at a point of levels crossing r_c with definite probability. Thus, the formulas obtained are applicable in a range of magnetic fields, where the level crossing occurs. However, in reality S$-$T$_-$ transitions proceed in a zone, the size of which depends on the values A, J_0, λ, and B_0. In very low magnetic fields this zone is strongly broadened. Therefore, the balance approximation becomes inapplicable. Also, it is possible to assume that the model discussed does not work at high fields, where the level crossing point disappears.

Anisotropy of Reactivity and Exchange Interaction. It is obvious that, in a general case, the exchange interaction in a radical pair, as the well as reactivity of radicals, is anisotropic and is determined by the distribution of spin density in the reacting particles. The reactivity anisotropy is defined by the steric factor f, the fraction of a radical surface favorable for the reaction:

$$f = \frac{\Delta S}{4\pi R^2} \quad (13)$$

Naturally, it would be averaged by translational and rotational motions of the radicals. In the simplest case, the effective shape of the crossing zone of energy levels is defined by the steric factor f_1, and for estimation, it can be assumed that $f_1 \approx f$. The reaction zone volume is

$$v = 4\pi \Delta R^2 f \quad (14)$$

and the rate of S$-$T$_-$ transitions in a level crossing region is[18]

$$K_c = \pi^2 r_c^2 \frac{a^2\lambda}{E} f \quad (15)$$

The function $g(r,R,s)$, which defines the kinematics of the relative motion of radicals in the pair, should be replaced with the function $g_1(r,R,s)$:[19]

$$g_1(r,R,s) = g^*(r,R,s+\tau_r^{-1}) + g(r,R,s) - g(r,R,s+\tau_r^{-1})$$

$$g^*(r,R,s+\tau_r^{-1}) =$$
$$\frac{\tau_p R}{r - R + R\sqrt{f}} \frac{\exp(-(r - R)\sqrt{(s + \tau_r^{-1})/D})}{1 + \sqrt{R^2 f(s + \tau_r^{-1})/D}} \quad (16)$$

where τ_r is the correlation time of modulation of the exchange interaction and reactivity anisotropy.

Anisotropy of the reactivity of radicals obviously affects the radical reaction rate in solution. This problem has been considered by Doctorov at al.,[19] and the following correction has been applied to formulas for the rate of a diffusion-controlled reaction for radicals with steric factor f:

$$k_d = \frac{8RT}{3000\eta} \frac{f}{\chi} \quad (17)$$

where R is the gas constant and

$$\chi = \frac{\sqrt{f}}{1 + \sqrt{f\tau_d/\tau_r}} + f\left(1 - \frac{1}{1 + \sqrt{\tau_d/\tau_r}}\right) \quad (18)$$

Discussion

Manifestation of S$-$T$_-$ Transitions in Low Magnetic Fields: A Qualitative Consideration. In the absence of a

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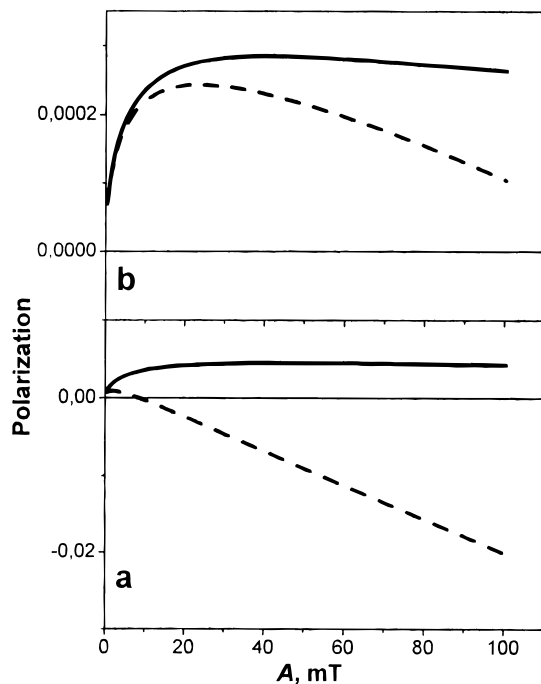
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Figure 3. Calculated in-cage CIDNP dependence on the HFI constant at $B_0 = A$, where solid line takes into account only S–T_0 (S–T_+, S–T_-) transitions and dashed line S–T_0 and S–T_- transitions: $J_0 = -450$ mT, $\lambda = 0.7$ Å: (a) $f = 1$; (b) $f = 0.08$, $\tau_r = 7$ps.

scavenger products **I** and **II** can be formed by both in-cage and escape routes. Thus, the observed CIDNP of these compounds consists of the following contribution to the polarization: (i) in-cage of geminate RP (P_{inc}), (ii) escaped from geminate or F-pair (P_{esc}), (iii) in-cage of diffusional RPs (P_F), and (iv) escaped from F-pairs that consist of two phosphonyl radicals ($P_{esc'}$). The sign of the CIDNP effect is determined by the sign of the sum of these four contributions: $P = P_{inc} + P_F + P_{esc} + P_{esc'}$.

The geminate polarization (P_{inc}) is formed as a result of singlet–triplet transitions occurring in a zone with zero exchange interaction, $P(S-T_0,S-T_+,S-T_-)$ (for brevity, $P(S-T_0)$), and polarization generated due to S–T_- transitions, occurring in a zone of crossing of $T_-\alpha$ and Sβ terms, $P(S-T_-)$. For a qualitative analysis one can write $P_{inc} = P(S-T_0) + P(S-T_-)$. For $A > 0$, $J < 0$, and the triplet precurcor of RP, $P(S-T_0) > 0$, $P(S-T_-) < 0$. If $|P(S-T_0)| < |P(S-T_-)|$, $P_{inc} < 0$; i.e., the geminate CIDNP has to be emissive. In the opposite case when $|P(S-T_0)| > |P(S-T_-)|$, $P_{inc} > 0$; i.e., the polarization of compound **I** should be absorptive. The change in intensity and in sign of geminate CIDNP calculated with and without the exchange interaction is demonstrated in Figure 3 as a function of HFI constant at a magnetic field equal to the HFI constant ($B_0 = A$). One can see that accounting for S–T_- transitions leads to a decrease in the CIDNP intensity; however, the CIDNP sign does not change. In the presence of scavenger, CIDNP of compound **I** corresponds to polarization formed only in geminate RPs. Thus, from experimental data one can conclude that the contribution to polarization from S–T_- transitions occurring in a zone of crossing of $T_-\alpha$ and Sβ terms is less than from S–T_0 (S–T_+, S–T_-) transitions.

The signs of CIDNP of in-cage products for triplet RP and the F-pair are the same:[13] $P_F = kP_{inc}$, $k > 0$. For polarization of escape products of geminate RPs one can write $P_{esc} = -\delta P(S-T_0) + \delta P(S-T_-)$, where $\delta < 1$ takes account of the nuclear relaxation in the intermediate radicals and the fact that only

some of the escaped radicals give the initial compound. In the case when in-cage and escape products are the same (photolysis without a scavenger) and δ is small, the contributions to CIDNP formed due to S–T_0 transitions are about equal, and thus, the net polarization is ~$2P(S-T_-)$. Thus, the emissive polarization observed in the absence of the scavenger can be caused by the significant but not the principal contribution of S–T_- transitions that occurs in the region of the $T_-\alpha$ and Sβ level crossings.

Quantitative Analysis of Experimental Data. The comparison of experimental and calculated data was carried out by fitting of the calculated shape of CIDNP magnetic field dependencies in various solvents. The following parameters were used in calculations: the g factors, HFI constant, the value of exchange interaction at contact radius J_0, parameter of the exchange interaction decay λ, radical lifetime, radical radius R, and diffusion coefficients of solvents. For radicals formed in the photolysis of **I**, $g_1 = 2.0018$, $g_2 = 2.0008$, $A \approx 70$mT,[6] and $R \approx 6 \pm 0.5$ Å (sum of radii of dimethoxyphosphonyl and trimethylbenzoyl radicals).

Since we could not find in the literature the rate constant of the reaction of the dimethoxyphosphonyl radical with CBrCl$_3$, we estimated it, using the values of rate constants of reactions of diethoxy- and diphenylphosphonyl radicals with benzylbromide, which are equal to, respectively, 0.012×10^8 M^{-1} s^{-1} [20] and 0.59×10^8 M^{-1} s^{-1}.[6] The rate constant of the reaction of the diphenylphosphonyl radical with CBrCl$_3$ is 8.3×10^8 M^{-1} s^{-1}.[6] Assuming an insignificant increase of reactivity of the dimethoxyphosphonyl radical in comparison with that of diethoxyphosphonyl, it is possible to estimate k_q for the reaction of the dimethoxyphosphonyl radical with bromotrichloromethane as 0.2×10^8 M^{-1} s^{-1}. One can assume that benzoyl radical reacts with the scavenger faster than phosphonyl. The value of the reaction rate constant of trimethylbenzoyl radical with CBrCl$_3$ was taken to be equal to 1×10^8 M^{-1} s^{-1}, on the assumption that it is less than the typical reaction rate constant of acyl radicals with CBrCl$_3$: ~1×10^9 M^{-1} s^{-1}.[21] Thus, we estimated the lower limit of the pseudo-first-order rate constant of the reaction of the trimethylbenzoyl radical with CBrCl$_3$ as $K_S = 1.2 \times 10^7$ s^{-1}.

The fitting parameters for the calculation of CIDNP ^{31}P magnetic field dependencies are the following: exchange interaction at contact radius J_0, decay parameter λ, and the parameter of the anisotropy of reactivity and exchange interaction f ($0 < f \ll 1$) and τ_r.

Calculation by Analytical Eqs 1, 2, and 16. Figure 4 shows the calculated CIDNP field dependencies in dioxane and acetonitrile in the presence of scavenger for different values of J_0 and λ without taking into account the anisotropy of exchange interaction ($f = 1$). One can see that the agreement between experimental and theoretical results is rather poor because of overestimation of the contribution of S–T_- transitions to CIDNP. The contribution of the S–T_- transitions can be decreased by decreasing the parameters of the exchange interaction J_0 and λ. However, for the reasonable values of parameters J_0 and λ taken from the literature,[22–24] 0.3 Å $\leq \lambda \leq$ 0.9 Å, 0.03 T$\leq J_0 <$ 570 T, it is impossible to obtain good agreement between experimental and calculated data. Similar shapes of experimental and calculated CIDNP dependencies can be achieved only by using $\lambda = 0.055$ Å, $J_0 \approx 150$ T, which are very far from the evaluated values for many systems.[22–24] The anisotropy of reactivity and exchange interaction produces good agreement between calculated and experimental data (Figure 2). The parameters of the best fit are $J_0 = -450 \pm 100$ mT, $\lambda = 0.7 \pm 0.1$ Å, $f = 0.08 \pm 0.02$, $\tau_r = 7 \pm 2$ ps (in CH$_3$CN), 25
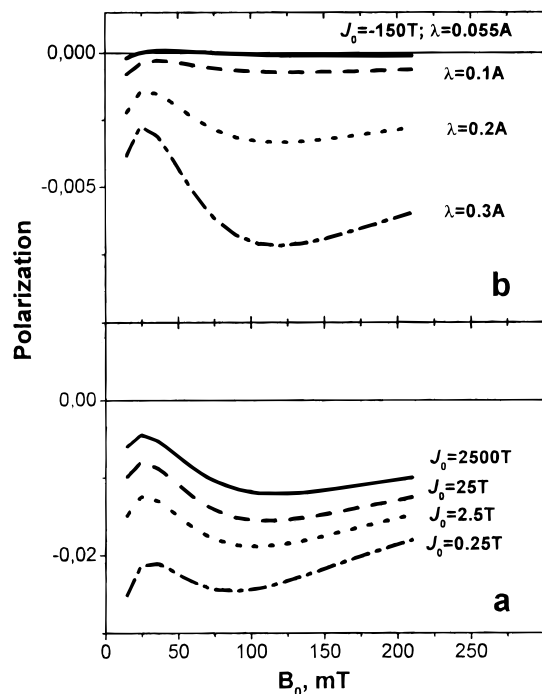
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Figure 4. Calculated CIDNP field dependencies in dioxane without taking into account anisotropy of exchange interaction: (a) variation of J_0, $\lambda = 0.4$ Å; (b) variation of λ, $J_0 = -2500$ T.

Figure 5. Effective S–T_ contribution to CIDNP upon the photolysis of **I** with $K_S = 1.2 \times 10^7$ s^{-1} (solid line) and $K_S = 0$ (dashed line).

± 3 ps (in dioxane). The parameter τ_r corresponds to the typical correlation time of rotation of small radicals in nonviscous solvents and is close to the values published in ref 3. Note that the ratio of the correlation times obtained in CH$_3$CN and dioxane is equal to the ratio of the corresponding viscosity coefficients (0.357 and 1.255 cP). The parameters J_0 and λ obtained are very close to those previously obtained for a number of radical pairs. It is obvious that significant spatial heterogeneity of reactivity and exchange interaction should be expected in both radicals of the RP because of insignificant delocalization of spin density on the benzene ring in trimethylbenzoyl and on the methoxy groups in the dimethoxyphosphonyl radical. The insignificant values of HFI constants on nuclei ^{1}H in these radicals are in a good agreement with this. Therefore, the small value of the steric factor f is reasonable.

By use of the steric factor $f = 0.08$ obtained, the estimated by eqs 17 and 18 reaction rate constant of phosphonyl radicals in the solution is $k_d = 5 \times 10^9$ M^{-1} s^{-1}. This value is in a good agreement with the literature rate constant for two phosphonyl radicals or phosphonyl and benzoyl radicals in benzene:[25] (3– 5) $\times 10^9$ M^{-1} s^{-1}.

To estimate the contribution of S–T_ transitions in geminate CIDNP, we subtracted the CIDNP magnetic field dependence calculated, taking into account only S–T$_0$ transitions from the optimized theoretical curve. The evaluated contributions of CIDNP due to the S–T_ mechanism for compound **I** in acetonitrile and dioxane are shown on Figure 5. The relative contribution of CIDNP due to the S–T_ mechanism in nonviscous solutions does not exceed 50%, and absorptive CIDNP is observed. In highly viscous solvents (dioxane), for RPs with a large HFI constant, the contribution of S–T_ transitions in the level crossing zone is predominant (>50%); and one should expect emissive CIDNP in low magnetic fields independent of the sign of the HFI interaction. The scavenger reaction ($K_S < 1 \times 10^8$ s^{-1}) has an insignificant effect on the absolute CIDNP intensity of geminate RP or the relative
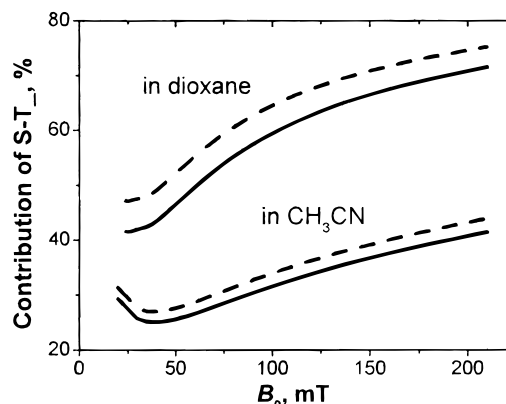
contribution of CIDNP due to the S–T_ mechanism (~7% in dioxane and ~3% in CH$_3$CN) (Figure 5).

Calculation by Numerical Solution of Stochastic Lioville Equation. In a previous paper[7] we have compared CIDNP field dependencies calculated by analytical formulas with those calculated by numerical solution of the stochastic Lioville equation (SLE) in a microreactor model.[26] In the latter case the diffusion of radicals in a homogeneous solution was modeled as a diffusion of one radical in a micelle of very large size, 400 Å, while the second radical was assumed to be fixed in the center. We used the scavenging rate constant $K_{scv} = 5 \times 10^6$ s^{-1} in order to fulfill the condition $1/K_{scv} < Z^{-1} < \tau_d$ (Z is the characteristic frequency of forced re-encounters $Z^{-1} = L^3/(3RD)$ and τ_d is the RP lifetime in the microreactor ($\tau_d = L^2/D$)). Qualitative agreement has been obtained between the experimental and calculated magnetic field CIDNP dependencies in solvents of different viscosity. However, although experimentally observed CIDNP in the absence of scavenger consists of the contributions from polarization of both in-cage products of geminate RPs and from escape products of geminate and diffusional RPs, only the contribution of in-cage products of geminate RPs has been taken into account in the calculations. Therefore, the parameters of the exchange interaction obtained in ref 7 are not correct. The CIDNP measured in the presence of the radical scavenger arises from only in-cage products of geminate RPs, and this allows us to make the correct comparison of experimental and calculated data. Obviously, K_{scv} used in the calculations corresponds to the pseudo-first-order rate constant of radicals with scavenger K_S. Figure 6 demonstrates calculated CIDNP field dependencies for the photolysis of compound **I**. Satisfactory agreement between experimental and calculated data can be achieved using the following values: $J_0 = -150$ T, $\lambda = 0.125$ Å. To account correctly for the exchange interaction, a micelle with radius 200 Å was divided into 10 000 shells according to the finite-difference scheme of Pedersen and Freed.[27] It should be noted that the shape of the CIDNP field dependence in this region of values of 0.5 T $< J_0$ and $\lambda < 0.4$ Å does not depend on the parameter $k_s\tau$, which corresponds to the recombination probability of singlet RP in the first shell, and only the magnitude of CIDNP is proportional to $k_s\tau$.

The value of J_0 is more that 150 times larger, and that of λ is 4–5 times less, than those previously obtained from the fitting of CIDNP, SNP, and TR ESR experimental data of similar RPs in micelles.[23,24] Moreover, neither numerical nor analytical calculations of CIDNP in homogeneous solutions using the parameters optimized in ref 24 ($J_0 = -90$ mT, $\lambda = 0.4$ Å) leads to agreement with the experimental results (Figure 7). It is reasonable to assume that the averaging of the exchange
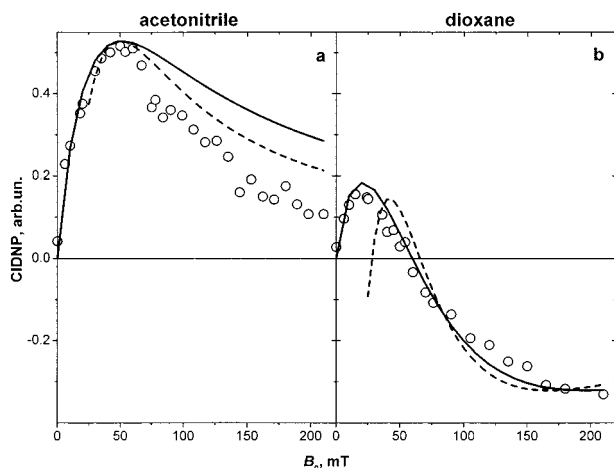
Figure 6. Comparison of CIDNP field dependencies calculated by numerical solution of the SLE (solid line, $J_0 = -150$ T, $\lambda = 0.125$ Å, $k_s\tau = 1$) and by analytical formulas without exchange interaction anisotropy (dashed line, $J_0 = -150$T, $\lambda = 0.055$ Å): (○) experimental curves.
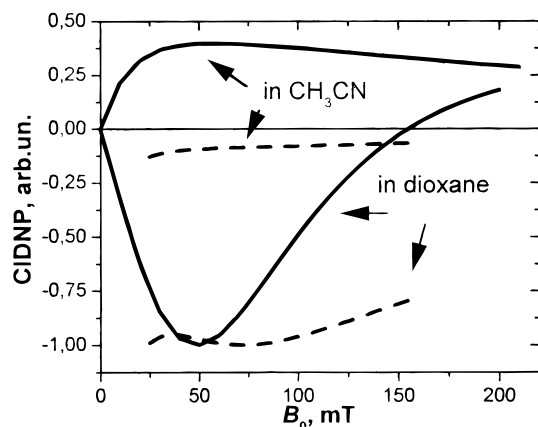

Figure 7. CIDNP field dependencies calculated by numerical solution (solid line) and by analytical formulas without exchange interaction anisotropy (dashed line) with exchange interaction parameters obtained in ref 24 ($J_0 = -90$ mT, $\lambda = 0.4$ Å). All curves are normalized to CIDNP intensity in dioxane.

interaction anisotropy in a micellar solution is more effective because of the substantially longer lifetime of micellized RPs in comparison with those in homogeneous solution and because of the larger number of radical re-encounters in the micelle. The averaging in homogeneous solution is less effective. It should be noted that the model of homogeneous solution for a micelle with a large radius is not quite correct. However, at present the stochastic Liouville equation for a homogeneous solution, taking into account the distance-dependent exchange interaction, has not been solved. It is possible to take account of the exchange interaction anisotropy in a microreactor model, but this leads to a significant increase of the computing time and therefore has also not been done.

The best agreement that can be achieved between the shapes of CIDNP magnetic field dependencies calculated by the two models, without taking into account the anisotropy of the exchange interaction, and experimental data is shown in Figure 6. The value of J_0 is the same for both models, while there is a factor of 2 difference in the parameter of exchange decay: $\lambda = 0.055$ Å for the balance approximation and $\lambda = 0.125$ Å for the numerical solution. In our opinion this difference reflects the main defect of the balance approximation in modeling real level crossing region by crossing at one point. However, a

comparison of calculations made for both models shows that the analytical solution predicts the main peculiarities of the CIDNP quite correctly and proves the applicability of the balance approximation.

CIDNP on Other Products. Product **II** can be formed in geminate RP as well as in F-pairs. The presence of scavenger cuts off the route of F-pair formation and leads to a shortening of the RPs' lifetime. Just after α-cleavage the phosphoryl oxygen in the dimethylphosphonyl radical remains space-hindered,[28] which leads to the very low O-recombination rate. With the lapse of time, space hindrance is eliminated and the possibility of O-recombination appears. Thus, the presence of scavenger affects the O-recombination rate constant much more than P-recombination. This fact leads to a decrease of the ratio of product yields **II/I** in the geminate RP in the presence of scavenger.

The net CIDNP of compounds **III** and **IV** has contributions from both escape polarization of geminate RP and in-cage polarization formed in F-pairs of two phosphonyl radicals. The quantitative analysis of CIDNP of RPs with two large HFI constants is complicated in low magnetic fields. Therefore, we shall make only qualitative remarks. It is obvious that the S−T− transitions for such RPs are more effective than for RP with one HFI constant. The CIDNP of RPs that consist of two phosphonyl radicals should be equal to zero in a high magnetic field. Thus, the CIDNP of products **III** and **IV** corresponds to the escaped polarization of geminate RPs and should be emissive.[10] However, the CIDNP obtained on **III** is absorption at 2.1 T in acetonitrile. The only explanation of the observed sign of CIDNP is the contribution to CIDNP formed due to S−T+, S−T− transitions, which proceed in the zone of zero exchange interaction. These transitions have to be taken into account for the RPs with a high value of HFI interaction also in 2.1 T. The same conclusion has been drawn in ref 29, where it was shown that the S−T+ and S−T− transitions are responsible for the formation of the net CIDNP effect in the symmetrical RP of two tin-centered radicals ($A \approx 160$ mT) in 2.1 T. The CIDNP effect caused by S−T+ and S−T− transitions is probably compensated in dioxane by the effect of S−T− transitions in the level crossing region.

Conclusion

The CIDNP upon the photolysis of 2,4,6-trimethylbenzoylphosphonic acid dimethyl ester in solvents of different viscosities has been studied in high and low magnetic fields. It is shown that the correct analysis of CIDNP for RPs with large HFI constants requires taking careful account of all the ways of polarization formation (in-cage, F-pair, escaped).

The analytical formula obtained for calculation of CIDNP magnetic field dependencies, taking into account S−T− transitions in a level crossing zone in the balance approximation, the reaction with a scavenger, the anisotropy of exchange interaction, and the reactivity of radicals, describes experimental results well with the following set of parameters: $J_0 = -450 \pm 100$ mT, $\lambda = 0.7 \pm 0.1$ Å, $f = 0.08 \pm 0.02$, $\tau_r = 7 \pm 2$ ps (in CH$_3$CN), 25 ± 3 ps (in dioxane).

The comparison of calculated CIDNP field dependencies both by analytical formulas and by a numerical solution of a stochastic Liouville equation in a microreactor model showed satisfactory agreement between these two models. This allows the use of the analytical calculation for estimation of the main parameters that characterize the influence of the exchange interaction on the formation of CIDNP.

On the basis of comparison of the experimental and calculated CIDNP dependencies, it has been shown that the S−T$_0$ (S−

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T_+, $S-T_-$) transitions are mainly responsible for the formation of the net CIDNP of ^{31}P in the geminate pair of trimethylbenzoyl–dimethoxyphosphonyl radicals in a low magnetic field in acetonitrile (60–70% of $S-T_0$), while in dioxane the contribution of CIDNP formed due to transitions occurring in the $S-T_-$ level crossing zone is predominant (50–80% of $S-T_-$). The main contribution to CIDNP in a magnetic field of 2.1 T is caused by $S-T_0$ ($S-T_+$, $S-T_-$) transitions with a small $S-T_-$ contribution in solvents of high viscosity.

Experimental Section

2,4,6-Trimethylbenzoylphosphonic acid dimethyl ester (**I**) was synthesized as described in ref 30. Protonated acetonitrile and dioxane were obtained from "Reachim", Russia. Deuterated acetonitrile was obtained from Russian Scientific Centre "Applied Chemistry", and deuterated dioxane was obtained from "Izotop", Russia. Acetonitrile was distilled over P_2O_5. Dioxane was purified by distillation over KOH and then over sodium in Ar atmosphere. Only freshly distilled solvents were used.

The experimental low-field CIDNP setup is described in detail elsewhere.[31] The reaction mixture was irradiated by laser pulses (Lambda Physics) (308 nm, 20 Hz, energy 30–40 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 3 s. The high-field CIDNP experiments were carried out on a JEOL FX90Q NMR spectrometer by irradiation with a high-pressure mercury lamp.

In low-field CIDNP experiments, the concentration of **I** was 0.0039 M and the concentration of $CBrCl_3$ was 0.117 M; in high-field experiments the concentrations of **I** and $CBrCl_3$ were 0.012 and 0.36 M, respectively.

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