Chemically induced electron-nuclear spin polarization in zero and very low magnetic fields

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Chemically induced electron-nuclear multiplet spin polarization of transient radicals at very low and zero magnetic fields has been observed. The photolyses of 2,4,6-trimethylbenzoyl phosphonic acid dimethyl ester and 2,4,6-trimethylbenzoyl diphenylphosphine oxide were used as a source of dimethoxyphosphonyl and diphenylphosphonyl radicals, which were detected using a modified L-band time–resolved electron paramagnetic resonance (TREPR) setup. TREPR spectra and time-resolved kinetics at low and high magnetic fields have been measured. The observed polarization is very strong. A theoretical description for the formation of this large polarization has been proposed and found to be in good agreement with experimental data.

Introduction

Chemically induced electron spin polarization (CIDEP) of reactive radicals is a well known phenomenon extensively investigated in high magnetic fields during last decades. At low magnetic fields, particularly those fields which are comparable to the hyperfine coupling constants of the radicals, the resonant transitions are not purely electronic or nuclear due to the mixing of wavefunctions. Recently it has been shown that low field electron-nuclear transitions can be detected *via* nuclear polarization of the diamagnetic products.[1)] These experiments revealed very high non–equlibrium populations of the spin levels in magnetic fields comparable to and lower than the value of the HFI constants of the intermediate radicals ($\gamma_e B_0 < a$). In this review we briefly introduce the results of first experiments involving direct measurement of low magnetic field chemically induced spin polarization using TREPR, as well as the theory for formation and decay of this polarization.[2, 3)]

Theory

The eigenfunctions and eigenstates for a radical containing one magnetic nucleus ($I = 1/2$) with HFI constant a are expressed by the Breite-Rabi formulas:[4)]

$$\begin{aligned}
&\Psi_1 = \alpha_e\alpha_n, && E_1 = \omega_e/2 + a/4,\\
&\Psi_2 = C_1\alpha_e\beta_n + C_2\beta_e\alpha_n, && E_2 = -\alpha/4 + (1/2)({\omega_e}^2 + \alpha^2)^{1/2},\\
&\Psi_3 = \beta_e\beta_n, && E_3 = -\omega_e/2 + \alpha/4,\\
&\Psi_4 = C_2\alpha_e\beta_n - C_1\beta_e\alpha_n, && E_4 = -\alpha/4 - (1/2)({\omega_e}^2 + a^2)^{1/2},
\end{aligned} \tag{1}$$

where ${C_1}^2 = (1/2)(1 + \omega_e/({\omega_e}^2 + a^2)^{1/2})$, ${C_2}^2 = (1/2)(1 - \omega_e/({\omega_e}^2 + a^2)^{1/2})$. Here $\omega_e = \gamma_e B_0$ is the Zeeman frequency of the electron, γ_e is the electron gyromagnetic ratio.

The initial spin level populations of the radicals escaped to the bulk strongly depend on the conditions under which the radicals have separated, and this affects the magnitude of the geminate electron-nuclear polarization. The separation can be adiabatic or non-adiabatic depending on the radical size, solution viscosity, and the HFI constants. The criterion of adiabacity can be written as $\lambda^2/D \sim a^{-1}$, where a is the HFI constant, D is the mutual diffusion coefficient, and λ is the characteristic scale for exponential decay of the exchange interaction in its usual form: $J(r) = J_0 \cdot \exp(-(r - R)/\lambda)$ (R is the distance of closest radical approach). We now consider the formation of low-field electron-nuclear polarization for two limiting cases of adiabatic ($\lambda^2/D >> a^{-1}$) and non-adiabatic ($\lambda^2/D << a^{-1}$) RP separation.

In the case of adiabatic separation the population of each eigenstate remains the same at any moment of time, though the eigenfunctions themselves change significantly. This allows us to predict the initial populations of RP spin levels in a low magnetic field using the simple energy level scheme shown in Fig. 1. Assume that RP is formed from a triplet state, i.e. 6 upper spin levels are equally populated. For the case when $a >> \gamma_e B_0$, after adiabatic RP separation to the region where $J = 0$, the 6 upper spin levels also have equal populations and the 2 lower levels are empty. This results in a large polarization of radical A with magnetic nucleus, as shown in Fig. 1. However, for radicals with HFI constants of 1–2 mT in non-viscous solutions, the adiabatic contribution is negligible, but it can be important for RPs with large HFI constants in solutions of high viscosity, *e.g.* in micelles, and for radical ion pairs.

In the case of non-adiabatic separation of radicals the calculation is rather cumbersome.[2, 3)] In zero magnetic field $\omega = 0$ the populations of spin levels of radical A with magnetic nucleus can be written as:

$$\begin{aligned}
n_1 = n_2 = n_3 &= 1/4 + (1/48)(a\tau_j/2)^{1/2}\\
&\quad \cdot (-\pi s_{aj} + R/\lambda + \ln|J_0\tau_j| + 2\gamma),\\
n_4 &= 1/4 - (1/16)(a\tau_j/2)^{1/2}\\
&\quad \cdot (-\pi s_{aj} + R/\lambda + \ln|J_0\tau_j| + 2\gamma),
\end{aligned} \tag{2}$$

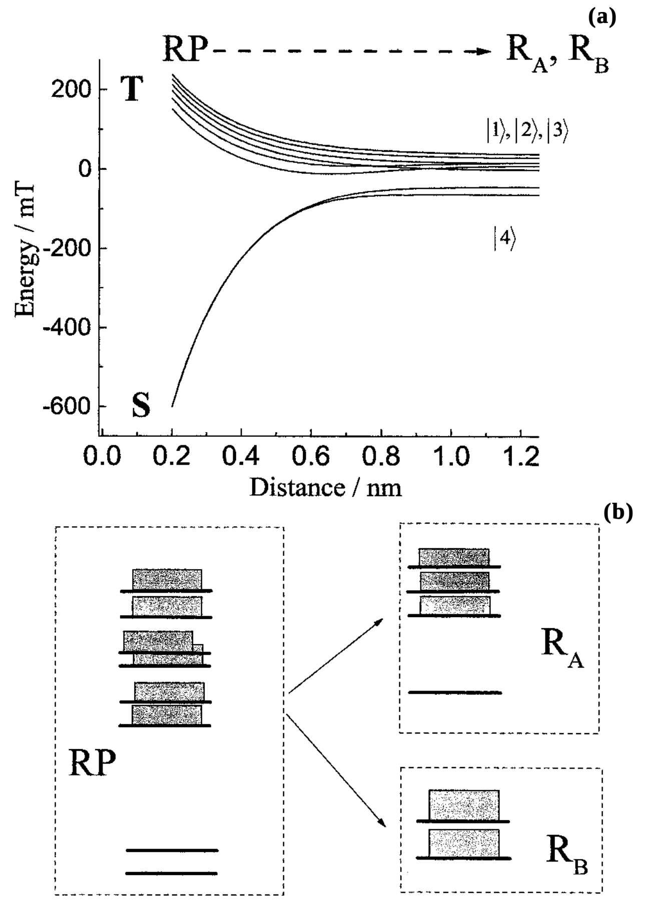

Fig. 1. Calculated scheme of the energy levels of RP with one magnetic nucleus as a dependence on interradical distance, $J(r) = J_0 \exp(-r/\lambda)$, $J_0 = 200\,\mathrm{mT}$, $\lambda = 0.05\,\mathrm{nm}$, $a = 70\,\mathrm{mT}$, $B_0 = 10\,\mathrm{mT}$ (on the top). The correlation scheme for the RP and radicals level populations (on the bottom).

where $s_{aj} \equiv \mathrm{Sign}\,(a \cdot J)$, $\tau_j = \lambda^2/D$, and $\gamma \cong 0.577$ is the Euler constant.

For a HFI constant of 70 mT (corresponding to the dimethoxyphosphonyl radical used in our experiments), assuming $R = 0.4\,\mathrm{nm}$, $\lambda = 0.05\,\mathrm{nm}$, $D = 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$ and $\ln|J_0\tau_j| \sim 1$, we calculate $\tau_j = 2.5\,\mathrm{ps}$ and $n_1 = n_2 = n_3 = 0.284$, $n_4 = 0.147$. Thus, at zero magnetic field $n_1 - n_4 = n_2 - n_4 = n_3 - n_4 = 0.137$, while $a/kT \sim 10^{-4}$. This means that a large emissive line should be observed, corresponding to transitions $\Psi_{1,2,3} \leftrightarrow \Psi_4$ with non-equilibrium populations of the spin levels.

Experimental

In this study we have created RPs using photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMBDPO) and 2,4,6-trimethylbenzoyl phosphonic acid dimethyl ester (TMPDE). Both compounds undergo α-scission upon irradiation with UV light with $\phi(\alpha) = 0.6$ for TMBDPO and $\phi(\alpha) = 0.3$ for TMPDE. The scission occurs from the excited triplet state and forms triplet radical pairs of phosphonyl and acyl radicals. Chemical decay of the intermediate radicals is determined by the recombination rate of radicals in the bulk. The radical $(\mathrm{Ph})_2(\mathrm{O})\mathrm{P}\bullet$ has a large HFI constant $a[^{31}\mathrm{P}] \approx 36.5\,\mathrm{mT}$ and small hyperfine coupling constants ($\leq 0.1\,\mathrm{mT}$) for the protons on the phenyl groups. The radical $(\mathrm{CH_3O})_2(\mathrm{O})\mathrm{P}\bullet$ has a large HFI of $a[^{31}\mathrm{P}] \approx 70\,\mathrm{mT}$ and small HFI constants $a[^1\mathrm{H}] = 0.05\,\mathrm{mT}$ for the six methyl protons. It is the large value of the HFI constant of the ^{31}P nucleus that allows us to use L-band TREPR with resonance frequency in the region between 1 GHz and 2 GHz for investigating the transitions at very low and zero magnetic fields.

A Jeol L-band TREPR setup has been modified for these measurements. To increase the sensitivity a GaAs MW amplifier (Miteq AMF-4F-011018-04-13P) has been inserted before a Double balanced mixer detector. The TREPR signal was amplified by a wideband preamplifier (0.5 Hz–50 MHz). Homemade loop gap resonators with an approximate Q factor of 200 were used to obtain a balance between high sensitivity and fast time resolution. In order to measure the signals at zero magnetic field, the resonant frequencies of the cavities were fine-tuned over ranges of about 10 MHz by changing the distance between the copper plate and the capacitive split in the resonator.

Results and discussion

Figure 2 shows TREPR kinetics measured for both emissive and absorptive lines of dimethoxyphosphonyl radical. It has been found that the kinetics of the low-field emissive line decays much slower than the high-field line at the same laser light intensity. The decay at high-field is monoexponential, whereas the decay at low-field is better described by second-order kinetics. This can be explained by the nature of HFI-induced spin relaxation at low fields, and is in complete agreement with our recent theoretical paper.[5] It was shown there, that at low field the relaxation rate between the lower and 3

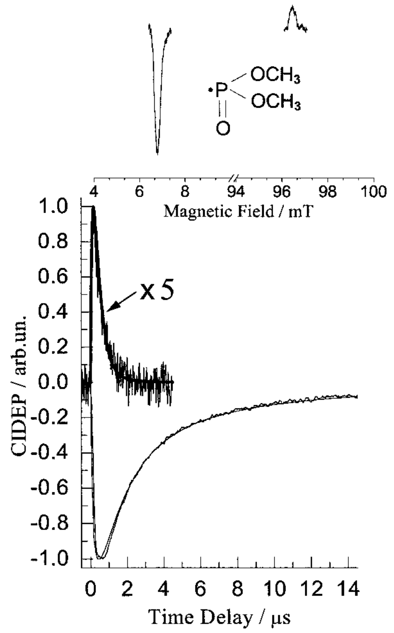

Fig. 2. The CIDEP spectra of dimethoxyphosphonyl radical $(\mathrm{MeO})_2(\mathrm{O})\mathrm{P}\bullet$ in acetonitrile at room temperature in L-band. Experimental kinetics and simulation of the CIDEP kinetics detected by the high-field and low-field EPR lines.

upper spin-levels ($\Psi_{1,2,3} \leftrightarrow \Psi_4$) is expected to be very slow in comparison with that at high field. The HFI-induced relaxation rate between levels $\Psi_{1,2,3} \leftrightarrow \Psi_4$ decreases to zero at zero magnetic field, because relaxation transitions induced by dipole-dipole interactions are not allowed between states that have different total spin.

Based on the results from Ref. 5, using $a = 70\,\mathrm{mT}$, a fluctuation amplitude due to hyperfine anisotropy, $[A{:}A] = 176\,\mathrm{mT}^2$, and $\tau_c = 2.4\,\mathrm{ps}$, we estimate that the HFI induced relaxation time will be $\sim 500\,\mu\mathrm{s}$ at $B_0 = 4.4\,\mathrm{mT}$. Therefore, we conclude that the high-field TREPR kinetics shown in Fig. 2 are determined by HFI-induced spin relaxation, while the low-field kinetics are determined by chemical reaction.

These conclusions have been confirmed by the calculated kinetic traces shown in Fig. 2, which were generated using a numerical solution of the Stochastic Liouville equation *via* a Laplace transform. The correlation time for radical rotation and the initial radical concentration were the variable parameters. Both kinetic traces shown in Fig. 2 were calculated using the same set of parameters. The correlation time of 2.4 ps used in simulation agrees well with that determined for the $(\mathrm{EtO})_2(\mathrm{O})\mathrm{P}\bullet$ radical in di-tert-butyl peroxide ($\sim$5 ps).[6, 7]

Finally, we emphasize that strong electron-nuclear polarization is detected in zero magnetic field. Figure 3 shows the spectra of $(\mathrm{CH_3O})_2(\mathrm{O})\mathrm{P}\bullet$ radical observed using rf-frequencies close to the values of the HFI constants. The magnetic field was swept gradually from –1.0 mT to 1.0 mT to detect the resonant transition at zero magnetic field. The observed lines correspond to the transition $\Psi_1 \leftrightarrow \Psi_4$ when $f > f_{\mathrm{hfi}}$, and to the transition $\Psi_3 \leftrightarrow \Psi_4$ when $f < f_{\mathrm{hfi}}$. The intensities of these transitions have been discussed in Ref. 2. It is clear that strong emission is observed at zero magnetic field for both radicals, in complete agreement with the predictions of Eqs. (2).

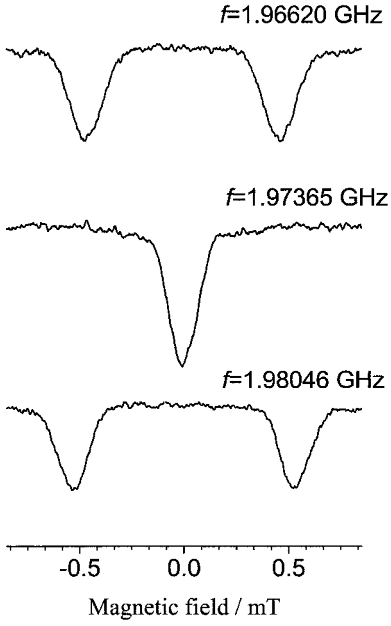

Fig. 3. Experimental CIDEP spectra of dimethoxyphosphonyl radicals at low and zero magnetic field at different frequencies of applied rf-field.

Photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMBDPO) has also been studied. The main difference in the reactions of photolysis of TMPDE and TMBDPO is the lifetime of excited triplet molecule, which is much shorter for the latter, therefore the triplet mechanism can contribute to the observed spin polarization. Indeed, the CIDEP signal of trimethylbenzoyl radical which was not observed during TMPDE photolysis, has been detected during photolysis of TMBDPO. Analysis of the experimental spectra and kinetics of $(\mathrm{Ph})_2(\mathrm{O})\mathrm{P}\bullet$ radicals showed the same trends and features as for $(\mathrm{MeO})_2(\mathrm{O})\mathrm{P}\bullet$. The presence of TM is therefore not critical for the existence of low-field electron-nuclear spin polarization.

Conclusions

In conclusion we would like to note that despite the fact that electron-nuclear polarization has been detected for the specific case of radicals with large HFI constants, the proposed polarization mechanisms should also work for radicals with HFI constant of 1.0–2.0 mT, or for radicals with several HFI-constants. For a radical with more than one non–zero HFI constant, the situation is more complicated, but zero field electron-nuclear polarization should still be observable.

The existence of strong spin polarization at low and zero magnetic field, which can be detected using oscillating rf-fields, is an important result. It will allow us to investigate mechanisms and kinetics of chemical reactions, molecular and spin dynamics of short-lived radical intermediates in a new set of conditions.

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