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A ^{31}P-SNP study of the photolysis of (2,4,6-trimethylbenzoyl) diphenylphosphine oxide in micelles of different sizes

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Abstract

^{31}P stimulated nuclear polarization spectra and their dependence on time after photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide in micellar solution of sodium octyl- (SOS) and dodecylsulfate (SDS) are investigated and discussed in terms of the numerical solution of the stochastic Liouville equation for a microreactor model. The decay of the geminate radical pair is found to be about 2.5 times slower in SDS than in the SOS micelles due to a larger re-encounter rate in the latter one. Simulation of the experimental results further suggests $J_0 \approx -1.6 \times 10^{10}$ rad/s for the exchange interaction at contact distance, and an increasing micellar size with increasing radical size.

1. Introduction

In the last decade, magnetic spin effects in micellized radical pairs (RPs) have been studied in detail [1]. TR ESR [2,3], MARY [4] and stimulated nuclear polarization (SNP) [3,5–8] studies have allowed the determination of a variety of parameters of the micellized species. The information contained in the SNP spectra have been successfully [6–8] evaluated by using the numerical solution of the stochastic Liouville equation for a microreactor model. This approach has yielded simulations, which have adequately described most of the experimental data and have shown, that the spin dynamics in the pairs is largely determined by the electron spin exchange interaction between the partner radicals.

Till now, SNP effects have been investigated only for ^{1}H and ^{13}C nuclei of C- and O-centered radicals [9]. In this work, we apply the technique to pairs involving other radicals, and report SNP spectra and their kinetics of ^{31}P-centered radicals, which are formed by the photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMBDPO) in micelles of different sizes. ^{31}P-centered radicals possess a large hyperfine splitting, providing fast singlet–triplet conversion as well as fast electron spin relaxation due to its anisotropy. This causes certain peculiarities in the SNP spectra and their dependence on time. It will be shown also that these special features are satisfactorily described by the microreactor model for the micelles.

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2. Results

After UV excitation of TMBDPO in organic solvents [10–13] and aqueous micellar solution [14] the molecule undergoes α-cleavage of the C–P bond from its triplet state. In aqueous (D_2O) solutions of sodium dodecylsulfate (SDS) and sodium octylsulfate (SOS) micelles the photolysis of TMBDPO yields the following main products which show ^{31}P nuclear polarization (Fig. 1 and Scheme 1): regenerated TMBDPO (I), diphenylphosphine oxide (II), and diphenylphosphonic acid (III). Gas chromatography reveals the formation of 2,4,6-trimethylbenzaldehyde (IV) and 2,4,6-trimethylbenzoic acid (V) as additional main products of the photolysis, which are invisible to ^{31}P NMR spectroscopy. The same reaction products have been identified in a previous investigation of the TMBDPO photochemistry in proton donating solvents [11].

[31]P SNP spectra obtained after the photolysis of TMBDPO in SDS and SOS micelles are shown in Fig. 2. They have been determined from the nuclear polarization of the regenerated starting compound (I). The spectra exhibit three extrema, at ≈ 26 and 51 mT (absorptive) as well as at 68 mT (emissive). The splitting between 26 and 68 mT corresponds to the hfi constant $A(^{31}P) \approx 38$ mT in the diphenylphosphonyl radical [15–17] at a resonance frequency of 1530 MHz (taking into account the shift in second order high-field approximation). The maximum at ≈ 51 mT is a so-called false maximum

Scheme 1.

[18]. The phases of the SNP spectra (absorption at the low-field and emission at the high-field site) correspond to an in-cage diamagnetic product of a triplet precursor of the RPs [9,18] (with $A(^{31}P) > 0$ [15]). In the spectrum taken with SDS micelles the absorption is slightly more intense than is observed for the SOS system. The asymmetry of the spectra is caused by the comparable values of the external magnetic fields $B_0 = 20$–78 mT (resonance frequency $\nu = 1530$ MHz) and the hfi constant of the ^{31}P nuclei ($A(^{31}P)/B_0 \approx 1$–0.5).

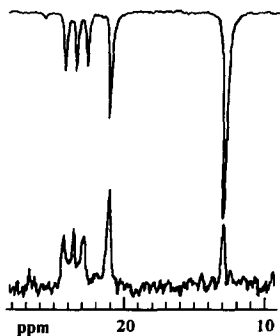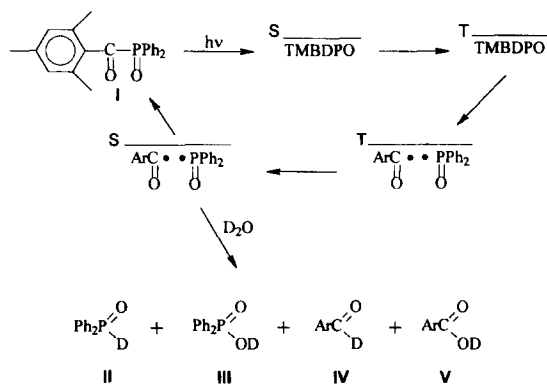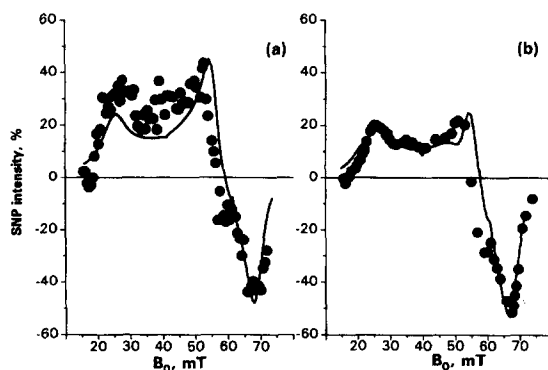Fig. 3 demonstrates the time dependences of the SNP signal of (I) in the SDS and SOS system. They

Fig. 1. CIDNP ^{31}P-NMR spectrum (top) (number of scans 4) and ^{31}P-NMR spectrum (number of scans 150) of the reaction mixture after photolysis (bottom) in SOS micelles. The singlet at 13 ppm corresponds to (I), at 21 ppm to (III) and the triplet at 24 ppm to (II).

Fig. 2. ^{31}P-SNP spectra ($B_1 = 2.3$ mT) for (I): (a) in SDS micelles, (b) in SOS micelles: (·) experimental data; (—) calculated for $J_0 = -1.6 \times 10^{10}$ rad/s, $1/\lambda = 2.5$ Å^{-1}, $R = 7$ Å, $L = 17.5$ Å (SDS) and 13.5 Å (SOS), ($A:A$) = 230 mT^2, $\tau_c = 45$ ps (SDS) and 30 ps (SOS); $D = 7 \times 10^{-7}$ cm^2/s (SDS) and 1.2×10^{-6} cm^2/s (SOS), $k_{esc} = 0.9 \times 10^6$ s^{-1} (SDS) and 1.3×10^6 s^{-1} (SOS). Experimental values are normalized to the CIDNP intensity at $B_0 = 64$ mT.

have been measured at the maxima of the emissive parts of the SNP spectra in Fig. 2 ($B_0 = 68$ mT). The decays are almost monoexponential within experimental error and yield decay rates of k_{obs}(SDS) = $(6.6 \pm 0.6) \times 10^6$ s^{-1} and k_{obs}(SOS) = (1.6 ± 0.4) $\times 10^7$ s^{-1} for the two micelles. Our value for k_{obs}(SDS) corresponds to a lifetime of the geminate radical pair of $\tau = 151$ ns, in satisfactory agreement with the result of a laser-flash photolysis study of TMBDPO in SDS micelles at zero magnetic field, which yielded $\tau = 139$ ns [14].

The literature data for the isotropic hfi constant of the ^{31}P nucleus in the diphenylphosphonyl radical range from 36.5 mT (in benzene [16]) to 37.3 mT (in propan-2-ol [17]), indicating a dependence on solvent. As the hyperfine interaction is one of the determining parameters in the simulation of SNP spectra, we have measured TR ESR spectra of this radical after photolysis of TMBDPO in an aqueous solution of sodium dodecylsulfate. The spectrum obtained 200 ns after the laser pulse is given in Fig. 4. The centre line and the additional doublet are assignable to the trimethylbenzoyl and phosphonyl radicals, respectively. The hfi constant of the latter is found to be $A(^{31}$P$) = (38.3 \pm 0.2)$ mT in the micellar environment. At short delay times after the laser flash the TR ESR spectrum exhibits a strong absorptive electron spin polarization, caused by the triplet mechanism [16,17,19], and a superimposed E/A polarization pattern. At longer delay times ($t \approx 400$–600 ns) the spectrum shows some antiphase structure, characteristic of spin correlated radical pairs [2].
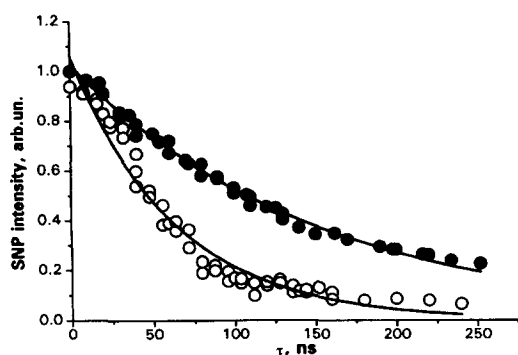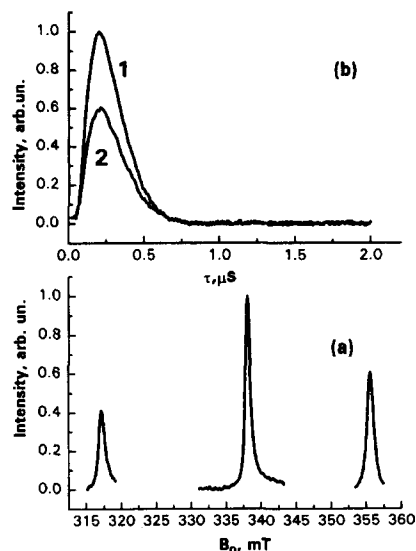

Fig. 4. TR ESR spectra after photolysis of I in SDS micelles: (a) time delay 200 ns, (b) TR ESR decays for trimethylbenzoyl radical (trace 1) and for the high-field line of the doublet of the phosphonyl radical (trace 2).

Fig. 4b shows the time dependences of the center-field line (trimethylbenzoyl radical, trace 1) and the high-field ESR signal amplitude (phosphonyl radical, trace 2). Their decay rates (in the monoexponential approximation) are 5.7×10^6 s^{-1} and 6.0×10^6 s^{-1} for the phosphonyl and trimethylbenzoyl radicals, respectively, very close to each other.

3. Discussion

3.1. SNP spectra

The splittings and linewidths in the SNP spectra have so far been found to be sensitive to the value of the exchange interaction and the rate of reaction between the partner radicals of micellized RPs [3,5–8]. The influence, these two parameters can have, should be determined mainly by the ratio A/Z [20], where A is the hfi constant and Z the rate of forced re-encounters. If $A/Z < 1$ the splitting is determined by the relative magnitudes of A, the exchange interaction J and the recombination probability $k_s\tau$. However, if $A/Z \gg 1$ the splitting in the SNP spectrum should be independent of J and $k_s\tau$, and just

Fig. 3. ^{31}P-SNP kinetics ($B_0 = 68$ mT, $B_1 = 1$ mT) for I in SDS micelles (($\bullet$) $k_{obs} = (6.6 \pm 0.6) \times 10^6$ s^{-1}) and in SOS micelles (($\circ$) $k_{obs} = (1.6 \pm 0.4) \times 10^7$ s^{-1}).

equal to the hfi constant A. In a previous work [3,5] we have studied RPs, composed of benzyl and benzoyl radicals (^{13}C-labeled in the carbonyl group), in micelles of different sizes (sodium heptylsulfate–sodium dodecylsulfate). There, the condition $A/Z \leq 1$ was met, and a significant decrease of the splitting in the SNP spectra with increasing exchange interaction (i.e. decreasing micelle size) was indeed observed. For the RP investigated in this work, the splitting in the SNP spectrum turns out to be essentially independent of the micelle size (see Fig. 2). Because of the large hfi constant of the ^{31}P nucleus we are here in the range $A/Z > 1$, where the exchange interaction can only slightly decrease the splitting in the SNP spectra, but mainly affects the linewidths.

As in our previous work [3,5,7], we have compared the experimental spectra in Fig. 2 with theoretical calculations based on the numerical solution of the stochastic Liouville equation for a microreactor model. According to this model, one radical is fixed at the center of a spherical micelle of radius L and the other freely diffuses in the micelle. It is assumed [1] that the exchange interaction decays exponentially with distance r, i.e.

$$J = J_0 \exp\left(-\frac{r-R}{\lambda}\right) \tag{1}$$

where R is the minimum inter-radical distance (contact radius), which is usually taken as the sum of the Van der Waals radii of the two radicals and λ represents the slope of the exponential decrease of J. We have taken $\lambda = 0.4$ Å and have estimated $R = 7$ Å, somewhat larger than our previous estimate $R = 6$ Å for the benzyl–benzoyl RP. The exchange interaction J_0 at contact distance was left as a fit parameter.

Other parameters which enter the microreactor model and need to be known for the calculation are the radii L of the micelles, the intramicellar relative diffusion coefficients D of the radicals, the rate k_{esc} of radical escape from the micelles, and the radical recombination probability $k_s\tau$ within the micelles. In addition, the anisotropy $(A:A) = \sum_i (A_{iso} - A_i)^2$ of the ^{31}P hfi must be known as well as the reorientational correlation time τ_c of the phosphonyl radical, in order to take into account electron spin relaxation

due to the diffusional modulation of the hfi anisotropy and electron dipole–dipole interaction [21,22].

The diffusion coefficients were calculated from those of the benzyl–benzoyl RP [23] taking into account the larger radii of the radicals in this study and assuming an unchanged intramicellar viscosity. This yielded $D = 7 \times 10^{-7}$ cm^2/s for SDS and 1.2×10^{-6} cm^2/s for SOS micelles. The hfi anisotropy $(A:A) = 230$ mT^2 could be taken from the literature [15,24]. In order to estimate k_{esc}, we considered the fact that the TR ESR spectrum showed the characteristic antiphase structure of a spin correlated RP after electron spin relaxation had about equalized the populations of the T_+ and T_- levels. Further, the ESR signals of both radicals decayed with about the same rate, although their spin relaxation times are different [16]. Thus, we conclude that the ESR signal decay is dominated by the intramicellar radical recombination and that the escape occurs somewhat slower than spin relaxation and recombination, yielding a rough estimate of $k_{esc} \approx 9 \times 10^5$ s^{-1} for SDS micelles. For SOS the escape rate was chosen according to the proportionality $k_{esc} \approx 1/L$. All calculations were performed for $k_s\tau = 1$, i.e. close to diffusion controlled recombination of the singlet state RPs.

We have varied the free parameters J_0, L and τ_c in reasonable ranges around values which we have obtained previously for these parameters for the benzyl–benzoyl RP [4,5,23,25]. Satisfactory agreement with the experimental spectrum (see Fig. 2) was achieved with $J_0(\text{SDS}) = J_0(\text{SOS}) = -1.6 \times 10^{10}$ rad/s, $L(\text{SDS}) = 17.5$ Å, $L(\text{SOS}) = 13.5$ Å, as well as $\tau_c(\text{SDS}) = 45$ ps and $\tau_c(\text{SOS}) = 30$ ps. If compared with the benzyl–benzoyl system, we find reasonable agreement with the values of J_0 and the correlation times obtained there ($J_0 \leq (1-2) \times 10^{10}$ rad/s, $\tau_c(\text{SDS}) = 56$ ps, $\tau_c(\text{SOS}) = 22$ ps [5]). A noteworthy difference is found with respect to the micellar radii L. The fits are sensitive to this parameter, because an increase in L narrows the calculated spectral lines, and a decrease of L reduces the intensity of the absorptive part of the SNP spectrum due to S–T$_-$ transitions. From our simulations we must conclude that $L(\text{SDS})$ and $L(\text{SOS})$ must definitely lie in the ranges 17–21 and 13–15 Å, respectively. For the benzyl–benzoyl RP in the same micelles, radii of $L(\text{SDS}) = 15.4$ Å and $L(\text{SOS}) = 10.3$

Å have been determined. This indicates that the micelles somewhat adapt themselves to the larger molecules, possibly by a higher aggregation number [26].

3.2. SNP kinetics

The time dependence of the SNP amplitude (Fig. 3) can be analyzed using a simple kinetic scheme which has been discussed elsewhere [5,27]. As has been shown [5], the experimentally observed decay rate k_{obs} includes the rate constants of relaxation k_r, recombination from the singlet state k_s and escape of the radicals from the micelles k_{esc}:

$$k_{obs} = k_r + k_s/4 + k_{esc} - \sqrt{(k_r)^2 + (k_s/4)^2} \qquad (2)$$

The relaxation rate $k_r = k_{hfc} + k_{dd}$ can be caused by modulation of the hfi anisotropy (k_{hfc}) and/or the electron dipole–dipole interaction (k_{dd}). If $k_s/4 \gg k_r$, the observed rate constant is $k_{obs} = k_r + k_{esc}$, whereas for $k_r \gg k_s/4$ the observed rate constant becomes independent of the relaxation rate and is determined by $k_{obs} = k_s/4 + k_{esc}$. It is noted that a more accurate theoretical model has previously been reported [7] and applied to the SNP kinetics in the high magnetic field approximation. However, this model is not applicable here because the hfi constant of the phosphonyl radical is comparable with B_0. In addition, the results of Refs. [5,7] show that in many cases the application of a simple kinetic scheme is fruitful.

Let us estimate the relaxation rate k_r. At a magnetic field of 68 mT, the electron relaxation due to the anisotropy of the g-factor can be neglected. The rate of radical recombination from the triplet-state RP, due to spin–orbit interaction, also seems to be negligible [28]. The dipole–dipole relaxation can be evaluated according to the literature [21,29]. For SOS micelles it is $(3-5) \times 10^5$ s^{-1} and for SDS this value is even lower and gives no considerable contribution to k_{obs}. Thus, in our case, the main mechanism of electron relaxation is the relaxation due to the hfi anisotropy. It can be estimated from [21]

$$k_{hfc} = \frac{\gamma_e^2}{12} \times \frac{(A:A)\tau_c}{1 + \omega^2\tau_c^2}. \qquad (3)$$

Taking the correlation times derived by simulation of the SNP spectra (45 ps in SDS and 30 ps in SOS), we obtain for the SDS micelle a relaxation rate $k_r \approx 3.5 \times 10^7$ s^{-1}.

The rate constant k_s for diffusion controlled recombination from the singlet state is determined by [6,30]

$$k_s \approx \frac{3RD}{L^3 - R^3} \qquad (4)$$

This gives a value of k_s of about 2.9×10^7 s^{-1} at $R = 7$ Å and $L = 17.5$ Å for SDS. The observed rate constant 6.6×10^6 s^{-1} is close to the value of $k_s/4$ including k_{esc}. Thus, according to Eq. (2), the observed rate constant for the photolysis of TMBDPO in SDS micelles is determined by the rate of recombination from the singlet state. For SOS micelles Eq. (3) yields a relaxation rate $k_r = 2.0 \times 10^7$ s^{-1}, only 1.8 times lower than that in SDS. The estimation of $k_s/4$ from Eq. (4) gives $k_s/4 = 3.0 \times 10^7$ s^{-1} for $D = 1.2 \times 10^{-6}$ cm^2/s and $L = 13.5$ Å, which is comparable with k_r. Thus, in SOS micelles the observed SNP kinetics are determined by both electron relaxation and recombination. The decay rate constant $k_{obs} = 1.6 \times 10^7$ s^{-1} measured in SOS micelles is about 2.5 times larger than for SDS and shows good agreement with the value 1.5×10^7 s^{-1} obtained from Eq. (2).

4. Experimental

(2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (BASF) was recrystallized from hexane; D_2O (Izotop, Russia) and sodium dodecylsulfate (Aldrich), were used as received. Sodium octylsulfate (Lancaster) was recrystallized from an ethanol–ether mixture.

After photolysis, solid barium chloride was added to the reaction mixture, the precipitate of barium dodecylsulfate was filtered off and extracted with benzene in a Soxhlet apparatus. The water filtrate was extracted with benzene, the organic layers were collected and dried by azeotropic distillation of water. The benzene solution was analyzed on a Varian 3400 gas chromatograph interfaced with a Finnigan MAT ITD 800 mass spectrometer. The separation was performed on a 30 m fused silica column (wide

bore 0.25 μm) containing SPB-5 with helium as a carrier gas (temperature range 70–250°C at a rate of 10°C min^{-1}).

For SNP experiments, 0.1 M (SDS) and 0.2 M (SOS) solutions of the detergent were used. The concentration of TMBDPO was 1 molecule per micelle (the aggregation numbers for SDS and SOS are 62 and 27, respectively [26]).

The experimental SNP apparatus has been described elsewhere [9]. The reaction mixture was irradiated by laser pulses (ELI (Estonia)) (308 nm, 20 Hz, energy 40–60 mJ/pulse, pulse duration 20 ns) in a mw resonator ($\nu = 1530$ MHz) located in the field of the magnet. A flow system was used to transfer the irradiated mixture to the probe of a Bruker MSL 300 NMR spectrometer. The time for transfer was 1 s and the residence time about 5 s. TR ESR spectra were obtained with the apparatus described in Ref. [31].

5. Conclusions

^{31}P SNP spectra and their dependence on time have been obtained after photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide in aqueous micellar solution.

The observed rate constant of RP decay in SDS micelles was found to be determined by the rate of radical recombination from the singlet state. The rate of RP decay in SOS micelles is about 2.5 times faster than that measured in SDS and is determined by a higher rate of re-encounters due to the smaller micelle size.

The numerical solution of the stochastic Liouville equation for a microreactor model was applied to the theoretical treatment of the experimental data. It was shown that the value of the exchange interaction for the RP of phosphonyl and benzoyl radicals is close to that obtained previously for carbon-centered radical pairs.

The effective sizes of the micelles for the RPs under investigation were found to exceed those for the previously investigated smaller carbon-centered RPs. This can be associated with an actual increase in the aggregation number of the micelles due to the presence of large molecules, as well as with differences in radical motion, which lead to differences in the rates of re-encounters.

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