

TIME-RESOLVED INVESTIGATION OF SINGLET RADICAL PAIR RECOMBINATION IN WATER-IN-OIL MICROEMULSIONS: MAGNETIC FIELD EFFECTS IN TWO TIME DOMAINS

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Geminate recombination of singlet radical pairs has been studied by nanosecond laser flash spectroscopy in nanometer-sized water droplets of AOT/H₂O/isooctane W/O microemulsions. The radical pairs were produced by electron-transfer quenching of singlet excited oxonine by N,N,N',N'-tetramethylparaphenylenediamine. Weak magnetic fields ($B_{1/2} = 7.5$ mT) decrease the yield of radicals appearing directly after the laser flash. In stronger fields an increase in the rate of time-resolved recombination from $k_{\text{rec}} = 1.1 \times 10^6 \text{ s}^{-1}$ at zero field to $k_{\text{rec}} = 1.8 \times 10^6 \text{ s}^{-1}$ at 1 T is observed. Onset of the latter effect occurs at about 50 mT. The dual magnetic field effect is discussed in terms of the CIDNP-type radical pair mechanism and the radical pair relaxation mechanism.

1. Introduction

In recent years a number of time-resolved observations of magnetic-field-dependent geminate radical pair recombination kinetics in micelles [1–10] and microemulsions [11–13] have been reported. It is remarkable to note, that all these investigations pertain to radical pairs produced from electronically excited *triplet* precursors. Since such radical pairs originate with triplet spin alignment their direct geminate recombination to singlet ground-state products is spin-forbidden. Spin evolution from triplet to singlet is necessary before recombination can take place, which is the reason why the effective recombination kinetics is sensitive to an external magnetic field.

It has usually been assumed that triplet-singlet conversion is the rate-determining step of triplet radical pair recombination and that it is the CIDNP-type mechanism, based on isotropic hyperfine coupling, which is responsible for the spin conversion process. The applicability of the CIDNP-type radical pair mechanism (which is characterized by a coherent spin evolution process) to the specific situation in micelles has been questioned by Hayashi and Nagakura who considered the contribution of the relaxation mechanism [3]. In our previous work

[11–13] on geminate radical pair recombination within nanometer-sized waterdroplets, henceforth termed nanodroplets[†], in W/O microemulsions we pointed out the importance of electron spin relaxation for the particular type of magnetic field dependence in such systems. We concluded that, in zero field, spin relaxation is probably faster than the spin-allowed recombination kinetics in the nanodroplet. As a consequence of these findings, one expects that radical pairs produced from excited singlet states should show a similar zero-field recombination kinetics as pairs produced from excited triplet states. The sign of the magnetic field effect, however, should be reversed with respect to the triplet case.

In this Letter we report the first time-resolved observation of magnetic field effects for *singlet* radical pairs in microphase supercages.

2. Experimental

Oxonine was a gift from Professor Dr. Kramer, University of Stuttgart. N,N,N',N'-tetramethylpar-

[†] This term, coined by Eicke [14], is more appropriate for the aggregates under consideration than "reversed micelles" which we used in our previous work.

aphenylenediamine (TMPDA) was synthesized according to ref. [15] and purified by repeated sublimation in vacuo. Sodium bis(2-ethylhexyl)-sulfosuccinate (AOT) from Fluka was purified as specified in ref. [16]. Isooctane (Fluka, puriss. p.a.) was purified by boiling with sulfonic acid for 2 h, then distilled, treated with a surplus of aqueous NH_3 for 20 min, washed five times with water and rectified. The purity was checked by GC. Demineralized water was distilled in a quartz apparatus. Methanol (Merck, p.a.) was used without further purification.

The W/O microemulsions were prepared by adding aqueous stock solutions of oxonine to isooctane containing AOT in a concentration of 0.04 M. The ratio of water to AOT was $c' = 16$. According to Eicke and Zinsli [17] the water core of the nanodroplets has a radius of about 30 Å under these conditions.

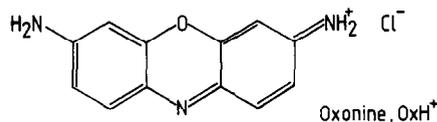
In both homogeneous methanolic solution and in microemulsion, the total dye concentration was 1×10^{-5} M. The concentration of TMPDA was 0.1 M in microemulsion and 2.7×10^{-2} M in methanolic solution in order to achieve 70% fluorescence quenching in both cases. Before the laser flash investigations, the solutions were flushed with N_2 for 30 min.

The kinetic investigations were performed with the nanosecond laser flash spectrometer described in ref. [13].

3. Results

In our previous experiments [11–13] thionine triplet has been used to produce triplet radical pairs in the aqueous nanodroplets of W/O microemulsions by means of an electron-transfer reaction with aniline and some of its derivatives. Thionine shows very efficient spontaneous triplet formation and is not well suited to produce singlet radical pairs because the excited singlet state is too short-lived and it would be hard to avoid that part of the radicals are formed from the excited triplet state. On the other hand, oxonine which is the S-oxa analogue of thionine shows negligible spontaneous triplet formation and is thus ideally suited to study singlet electron-transfer reactions in systems similar to our previous ones.

The efficiency of free-radical formation in elec-



tron-transfer reactions between oxonine singlet and various aromatic amines and methoxy compounds has been studied in homogeneous solution by Iwa et al. [18]. They established a linear correlation between the free enthalpy ΔG_{et}^0 of the electron-transfer process and the yield of free radicals. The radical yield increases with the exergonicity of the reaction. For our investigations we selected the donor TMPDA exhibiting the highest radical yield ($\Phi = 0.45$, $\Delta G_{\text{et}}^0 = -1.56$ eV) in the series of donors investigated by Iwa et al. [18]. The dye was solubilized in the polar microphase of a water/AOT/isooctane microemulsion containing suitable concentrations of the electron donor TMPDA (cf. section 2).

Water/AOT/isooctane microemulsions are well characterized in the literature [17,19] and have been used before as reaction media to study electron-transfer reactions [20,21].

In methanol the rate constant of the reaction between oxonine singlet and TMPDA has been reported to be $1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [18]. In microemulsion we found a Stern-Volmer-type behaviour of the stationary fluorescence intensity from which a quenching rate constant of $0.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ could be determined. The latter is about three times smaller than in homogeneous solution, indicating that there is some hindrance to the access of the electron donor molecules from the non-polar bulk phase into the polar interior of the nanodroplet, where the dye molecules are solubilized. In order to investigate the decay kinetics of the radicals produced in the quenching process, the TMPDA concentration was adjusted so as to achieve 70% fluorescence quenching in methanol and in microemulsion. The radical kinetics was followed at 413 nm where the observed absorbance is mainly due to the reduced semioxonine radical OxH[•] (cf. ref. [18]). The transient signals observed in homogeneous methanolic solutions and in microemulsion are shown in fig. 1.

During the presence of the laser pulse (half-width 10 ns) there is a strong transient absorption. This short-lived transient is also present in solutions with-

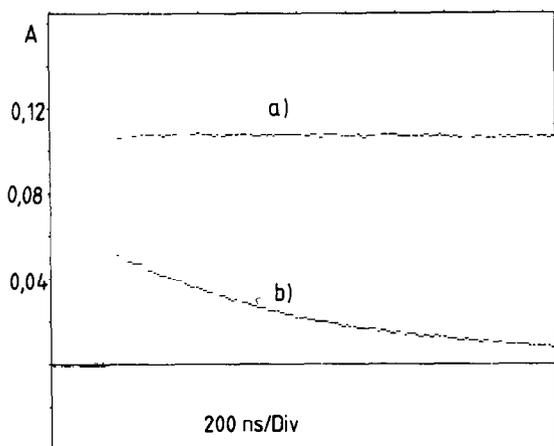


Fig. 1. Transient absorbance decay at 413 nm after laser flash excitation ($\lambda_{exc}=585$ nm) of oxonine ($c=10^{-5}$ M) (a) in methanolic solution with $c(\text{TMPDA})=0.027$ M and (b) in AOT/ H_2O /isooctane microemulsion with $c(\text{TMPDA})=0.1$ M. In both cases, (a) and (b), oxonine fluorescence quantum yield was quenched by 70%.

out quencher or in the presence of quenchers producing very low radical yield. It must be mainly attributed to S_1-S_n absorption of oxonine. However, a contribution from rapidly decaying geminate singlet radical pairs is probably included.

The radical decay kinetics observed after the laser pulse is markedly different in homogeneous solution and microemulsion. In homogeneous solution the decay during the first 2 μs is negligible (the radicals decay in a homogeneous second-order reaction with a rate constant of $2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ which is similar to the value reported by Iwa [22] of $2.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). On the other hand, in microemulsions the radicals disappear in an approximate first-order process with a rate constant of about $1.1 \times 10^6 \text{ s}^{-1}$. The latter process is clearly not attributable to bulk recombination but employs geminate radical pairs isolated in different nanodroplets (since the mean occupation number of nanodroplets by dye molecules amounts to only 5%, double occupations are negligible). The two signals in fig. 1 have been measured with the same laser pulse energy and at the same degree of fluorescence quenching. Thus the absorbance observed directly after the laser flash indicates that the yield of radicals at such a short delay time is clearly lower in the microemulsion. Using the free-radical quantum yield of 0.45 published by Iwa et al.

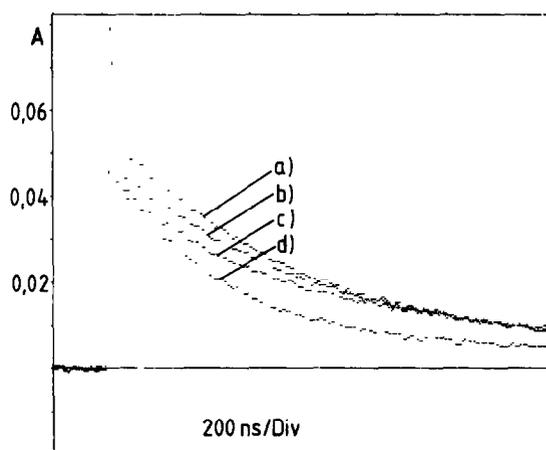


Fig. 2. Magnetic field dependence of signal (b) in fig. 1. Magnetic field strength: (a) 0 T, (b) 7.5 mT, (c) 50 mT, (d) 1 T.

[18] for methanol, we conclude from fig. 1 that the quantum yield of radicals surviving the first 10 to 20 ns within the polar microphase must be smaller than 0.25.

Magnetic field effect. Whereas in homogeneous solution a magnetic field effect on the signal is hardly detectable (the radical yield decreases by about 2%), significant effects arise in the microemulsion (cf. fig. 2). These may be described as a twofold magnetic field effect appearing in two different domains of time and magnetic field. At fields lower than 50 mT the radical yield observed after the end of the exciting laser pulse decreases, whereas the decay kinetics in the several-hundred nanosecond time domain is not yet noticeably affected.

The magnetic field dependence of the amount of radicals observed directly after the laser flash is shown in fig. 3. In order to minimize data scatter which may be caused by signal noise, the relative radical yields have been determined by employing an exponential fit of the decay curve after the laser flash and extrapolating back to an intersection with the fast decaying part of the absorbance signal during the laser pulse.

A second stage of the magnetic field effect occurs at fields higher than 50 mT and is borne out in the decay kinetics after the laser flash. Using a single-exponential fit we obtain a fairly constant value of $k=1.1 \times 10^6 \text{ s}^{-1}$ between 0 and 50 mT. This value starts to increase at fields higher than 50 mT. The value at 1 T, the strongest field applied, amounts to

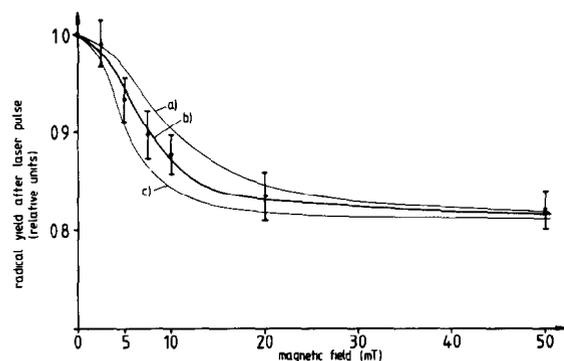


Fig. 3. Magnetic field dependence of radical yield detected directly after the laser pulse (cf. text). The solid curves are theoretical results (cf. text) obtained with parameter values (k_d, k_{tr}) yielding the observed high-field effect: (a) $13.5 \times 10^8 \text{ s}^{-1}$, $1.5 \times 10^8 \text{ s}^{-1}$ (b) $8.8 \times 10^8 \text{ s}^{-1}$, $1.2 \times 10^8 \text{ s}^{-1}$ (c) $4.4 \times 10^8 \text{ s}^{-1}$, $0.6 \times 10^8 \text{ s}^{-1}$.

$1.8 \times 10^6 \text{ s}^{-1}$. A limiting value does not seem to have been reached, however, at this field.

4. Discussion

4.1. Reaction scheme

The following observations are essential for establishing an appropriate reaction scheme:

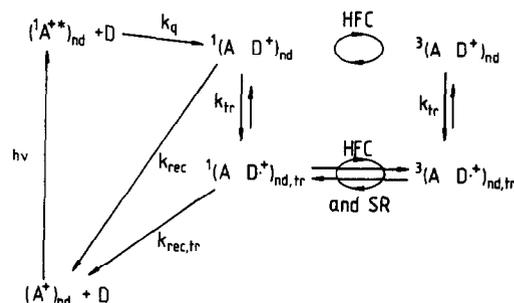
(i) The quantum yield of radicals determined directly after the laser pulse is considerably lower in microemulsions than in homogeneous solution (cf. fig. 1).

(ii) A magnetic field induces a significant decrease in the amount of radicals formed. This effect is saturated at low fields and is completely developed after 20 ns (duration of the laser pulse).

(iii) The radical decay observed after the laser pulse is much faster than in homogeneous solution and is accelerated by rather high magnetic fields.

A reaction model suggested in order to account for these features is depicted in scheme 1.

Geminate radical pairs with initial singlet spin correlation are produced in the polar interior of the nanodroplet (nd) by an electron-transfer reaction between the electron donor D and the singlet excited dye ($^1A^{*+}$)_{nd}, the latter being exclusively solubilized in the polar microphase whereby the specific site of solubilization (whether in the water core of the



Scheme 1.

nanodroplet or the polar interface) is open to discussion. It must be assumed that the initial re-encounter frequency of the radical pair in the nanodroplet changes drastically within a period which is short with respect to the duration of the laser pulse. The time resolution of our experiments allows an upper limit of about 3 ns to be assigned to this first stage of radical pair recombination. During this stage, the radical pair, designated as ($A^{\cdot-} D^{\cdot+}$)_{nd}, is characterized by a re-encounter frequency which must be higher than in homogeneous methanolic solution (cf. (i)) and/or extended over a longer period of time. Otherwise a sizeable magnetic field effect could not develop (cf. (ii)). A first-order rate constant k_{rec} is used to quantify the recombination rate in the first stage.

After at most a few nanoseconds the recombination rate of the radical pair must be drastically reduced by a process which we term a "trapping" process, with a rate constant k_{tr} . The justification for this assumption is that the recombination rate (rate constant $k_{rec, tr}$) is still so fast that it cannot be attributed to an exchange between different nanodroplets (in that case we would have to introduce an escape process instead of our "trapping" process) and that the magnetic field effect indicates a singlet spin memory of the radical pair which would not be found for non-geminate recombination involving radicals from different nanodroplets. In the "trapped" state the radical pair is designated as ($A^{\cdot-} D^{\cdot+}$)_{nd, tr}. Radical escape from the nanodroplet seems to be of minor importance in this system.

Produced with singlet spin correlation, the radical pairs will tend to approach spin equilibrium by various mechanisms. Due to these processes the singlet character of the radical pairs will decrease towards

an equilibrium value of 1/4 with a corresponding reduction of recombination probability in successive re-encounters of the radical pair in the polar micro-phase. By applying an external magnetic field, singlet-triplet transitions in the radical pair will be impeded so that the singlet spin memory will prevail for longer times and the recombination rate of the radical pair will increase in a magnetic field. This effect is observed as a decrease of the yield of slowly decaying radicals, detected directly after the laser flash, and as an increase in the observed radical decay rate in the several-hundred nanosecond time region.

4.2. Magnetic field effect during the first 10–20 ns

Since the decay of the short-lived radical pairs is completed after a few nanoseconds, the spin conversion processes causing a magnetic field sensitivity must be correspondingly fast. In the radicals under consideration it is not likely that incoherent processes, responsible for spin relaxation, will be effective in such a short time. On the other hand, it is well known that coherent singlet-triplet transitions induced by the isotropic hyperfine coupling interaction typically occur within this time domain. Quantitative calculations of the electron spin motion due to hyperfine coupling in the radicals OxH[•] and TMPDA^{•+} have shown that a quasistationary singlet probability is obtained after about 10 ns [23].

According to Weller [24] $B_{1/2}$ values for the magnetic field effect caused by the hfc mechanism in radical pairs obey the empirical relation

$$B_{1/2} = 2 \frac{B_1^2 + B_2^2}{B_1 + B_2}, \quad (1)$$

where B_1 and B_2 are the effective hyperfine fields of the radicals, given by

$$B_{(1,2)} = \left(\sum_{(i,1,2)} a_i^2 I_i(I_i + 1) \right)^{1/2}, \quad (2)$$

where the sum is extended over the magnetic nuclei of the corresponding radical. The validity of eq. (1) was demonstrated for radical pairs diffusing freely in homogeneous solutions. With $B_1 = 1.1$ mT for OxH[•] (here we used the same hfc constants as for the corresponding thionine radical [13]) and $B_2 = 2.5$ mT for TMPDA^{•+} (hfc constants used were rounded val-

ues from ref. [25]: $2 \times (a(\text{N}) = 0.7 \text{ mT})$, $12 \times (a(\text{CH}_3) = 0.7 \text{ mT})$, $4 \times (a(\text{H}) = 0.2 \text{ mT})$) a value of $B_{1/2} = 4.1$ mT is expected, whereas a value of $B_{1/2}(\text{exp}) = 7.5$ mT is obtained from fig. 3.

The discrepancy $\Delta B_{1/2}$ between the experimental $B_{1/2}$ value and the $B_{1/2}$ value according to eq. (1) of about 3.4 mT may be due to two effects:

(1) *Electron hopping*. In order to obtain a sizeable signal from the radicals the concentration of the electron donor had to be fairly high (0.1 M). Under these conditions hopping of the positive charge between different donor molecules cannot be excluded during the lifetime of the radical pair ($\text{A} \text{ D}^+$)_{nd}. In fact, $\Delta B_{1/2}$ values of similar magnitude have been observed by Staerk et al. [26] for pyrene and dimethylaniline ($c = 0.1$ M) in homogeneous solution. Unfortunately, because of low signal intensity in our system, it is difficult to lower the donor concentration further and to extrapolate to zero hopping rate.

(2) *Lifetime broadening*. Besides the hopping effect which itself can be considered as a lifetime broadening effect [26,27] frequent re-encounter within a definite radical pair will decrease the time span available for free spin evolution and thus cause higher $B_{1/2}$ values. Since the space available to the radical pair in the nanodroplet is rather restricted, its separation will often be within the distance where the exchange interaction J cannot be neglected. From the magnetic field dependence observed (cf. fig. 3) we can conclude that

$$J_{\text{eff}} < B_{1/2}(\text{hfc}).$$

Otherwise a level crossing effect with a maximum in the magnetic field dependence should have been observed, as has been shown by Weller and co-workers for a series of radical pairs connected by a covalent link of variable length [28]. Comparison of fig. 3 with the results of these authors indicates that effective spin evolution in our radical pairs ($\text{A} \text{ D}^+$)_{nd} occurs at interrational distances larger than 10 Å. On the other hand, Weller and co-workers have found that the $B_{1/2}$ values in linked radical pairs with $r_{\text{eff}} > 10$ Å may still be much larger than for freely diffusing radical pairs, which they attributed to the lifetime broadening effect of the linked radical pairs.

We have analyzed this lifetime broadening effect for our radical pairs by a model calculation based on the following assumptions:

– Spin evolution occurring between re-encounters can be described by the semiclassical method of Schulten et al. [29,30].

– The recombination probability in a re-encounter is equal to the actual singlet character p_S of the radical pair. Radical pairs separating from encounters are pure triplet pairs. (The generalisation to the case where an interruption of the spin evolution by exchange encounters occurs at a rate different than for recombination will be described elsewhere [23].)

– The sequence of re-encounters during the first kinetic stage can be described by an effective first-order process with a rate constant k_d . Furthermore a transition to the slow kinetic stage occurs with a rate constant k_{tr} .

The following expression for the yield of trapped radicals is obtained from this model:

$$\Phi_{tr}(B) = \frac{k_{tr}}{k_{tr} + k_d} \times \left(1 + \frac{3}{1 + k_{tr}/k_d \bar{p}_S(B, k_{tr} + k_d)} \right). \quad (3)$$

Here $\bar{p}_S(B, k_d + k_{tr})$ is the average singlet probability acquired by a radical pair between two successive encounters, if it separates with triplet spin after the first of these encounters. From eq. (3) the relative magnetic field effect on the yield of trapped radicals may be obtained for an arbitrary choice of the kinetic parameters k_d and k_{tr} . It is found that, whereas the amplitude of the magnetic field effect at high fields is mainly determined by the ratio k_{tr}/k_d , the half-field value of the theoretical field dependence is determined by $k_{tr} + k_d$. Thus it is a straightforward procedure to obtain a unique set of two parameters k_{tr} and k_d yielding a good fit to our experimental results (cf. fig. 3). These are

$$k_{tr} = 1 \times 10^8 \text{ s}^{-1}, \quad k_d = 9 \times 10^8 \text{ s}^{-1}.$$

Concerning the physical interpretation of the processes attributed to the rate constants k_d and k_{tr} , two principal possibilities are conceivable:

– The microenvironment of the radical pair in the nanodroplet might be rather viscous and the behaviour of the radical pair $(A \text{ } D^+)_{nd}$ might be typical of the situation of a geminate radical pair in a highly viscous homogeneous solvent. Whereas in homoge-

neous solution the fast geminate recombination phase is terminated by the separation of the geminate pair into the bulk solvent, in our case the radicals do not escape into the bulk after separating, but remain confined to the volume of the nanodroplet. The “trapping” process would then correspond to the loss of primary spatial correlation of the radical pair within the droplet where it has been produced.

– Another possibility is that for a short while after its production the radical pair or at least one of the radicals might be free to diffuse within the low-viscous water core, corresponding to a spherical volume of about 30 Å radius. For such a situation diffusion theory predicts a re-encounter frequency of the order of 10^9 s^{-1} . The “trapping” process would then have to be identified with an immobilization of both radicals probably in the surfactant/water interface region.

To obtain more information to decide between these two possibilities, experiments on the magnetic field dependence of the radical yield in highly viscous homogeneous solvents and in nanodroplets with different water core radii are in progress.

4.3. Kinetic magnetic field effect in the several-hundred nanosecond time regime

The time-resolved part of the geminate radical pair recombination shows a rate constant of $k_{rec, tr} = 1.1 \times 10^6 \text{ s}^{-1}$ in zero field which is by about three orders of magnitude slower than in the first stage of recombination. It seems very unlikely that it is a decrease of the specific recombination probability per singlet-radical-pair encounter which is responsible for the drastic decrease in the recombination rate constant after the first 20 ns of radical pair production. Rather we assume that the re-encounter frequency of the radical pair is decreased by some type of “trapping” of both of the radicals and that it is the decrease of the re-encounter frequency which is mainly responsible for the slowing down of the recombination kinetics.

Two models may be suggested for the re-encounter mechanism during the slow recombination phase:

(a) both radicals might diffuse slowly within the rather viscous water-surfactant interface and have their re-encounters there, or

(b) an adsorption-desorption equilibrium of the radicals between interface and water core may pro-

vide pathways for radical encounters in the interface via fast trajectories through the water core. At present a decision between these alternatives is not possible.

From the slow recombination kinetics it can be inferred that the time intervals between successive re-encounters are of the order of several-hundred nanoseconds. This is long enough to allow for an establishment of spin equilibrium between re-encounters, even if, in magnetic fields above 10 mT, the mechanistic contribution of the isotropic hyperfine coupling is quenched (cf. the corresponding situation for triplet radical pairs analysed in ref. [13]).

In magnetic fields exceeding 50 mT the recombination rate constant starts to increase, indicating that the singlet character of re-encounter radical pairs is higher than in zero field. From this observation one may conclude that at about 500 mT spin relaxation between T_{\pm} and T_0 or S drops below a rate of about $1 \times 10^6 \text{ s}^{-1}$. If it is completely suppressed one should expect that in high fields the radical pairs retain at least 50% singlet probability (only fast S- T_0 equilibration is possible) which is a factor of 2 higher than in zero field. Thus a maximum increase of the recombination rate constant by this factor should be expected. The maximum effect observed in our experiment corresponds to a factor of 1.64, but the magnetic field effect is not saturated at 1 T.

5. Conclusion

We have demonstrated that with the use of magnetic field effects two stages of recombination kinetics may be distinguished for geminate singlet radical pairs in the nanodroplets of W/O microemulsions. The first stage, which is completed after a few nanoseconds, is only detectable by the magnetic-field-dependent yield of radical pairs entering the second, time-resolved, recombination stage. Here fairly high magnetic fields lead to an increase in the recombination rate.

The two magnetic field effects are characteristic of two recombination stages with largely different re-encounter frequencies. In the short first stage the magnetic field dependence of the recombination yield is due to the well known CIDNP-type radical pair mechanism. In the slow second stage it is due to

magnetic-field-dependent spin relaxation, which has so far been observed for triplet radical pairs only [1-3,11-13]. Thus we have now demonstrated for radical pairs from singlet precursors, too, that in a magnetic field of 1 T the spin memory may prevail for several hundred nanoseconds.

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