MAGNETIC-FIELD DEPENDENT REACTIONS IN REVERSE MICELLAR SYSTEMS

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1. INTRODUCTION

In reverse micelles surfactant molecules enclose a polar core, where considerable amounts of water may be solubilized. For water/surfactant molar ratios (denoted as w) exceeding a value of about 10, the intramicellar water approaches the character of a thermodynamic microphase (1) distributed in fairly monodisperse droplets of up to several tens of nanometers radius. For these the term nanodroplets has been coined by Eicke (2). Since the water nanodroplets constitute potential microreactors, the radius of which may be easily controlled by w, we found them very attractive for investigating the recombination kinetics of spin-correlated radical pairs (RPs), which in homogeneous solution would predominantly undergo non-correlated second order recombination.

Studies of the magnetic-field dependence of kinetics and product yields of reactions involving radical pair intermediates have revealed the important aspect of electron spin correlation in radical pairs (3) during the period of time where diffusional geminate re-encounters take place. Such magnetokinetic effects are of great interest as a source of detailed information on the dynamics of radical pair reaction kinetics and how it is influenced by the medium. To understand the basis of magnetokinetic effects with radical pairs it is essential to recall that these 'remember' the spin alignment of their precursor state (singlet or triplet) for some time, even when they may have become separated to a distance where the exchange interaction between the unpaired radical electrons is zero. The loss of spin correlation in the radical pair which we will denote as 'spin evolution' may be due to two types of mechanisms: a coherent one, based on the difference in frequency and orientation of the axis of electron spin precession which the unpaired electron spins undergo in the different isotropic hyperfine fields of the two radicals, or an incoherent one which is due to stochastic motion of the two electron spins caused by fluctuating anisotropic

magnetic interactions, the same type of mechanisms which are also responsible for the linewidth of hyperfine lines in the esr spectra of individual radicals. The degree of spin evolution may be quantified in terms of time-dependent singlet or triplet character (p_S or p_T) of the radical pair, which will approach the values of 1/4 or 3/4, respectively, at times which depend on the strength of the interactions mentioned and on the strength of an external magnetic field, but typically will not exceed a few microseconds. At any time t after the radical pair has been created the value of p_S or p_T will be directly reflected by the recombination probability of the radical pair on a subsequent encounter at t. This probability is generally close to the value of $p_S(t)$ since radical pairs usually can only recombine to form products in their singlet ground states and do so at a rate which is usually diffusion-controlled. The yield of geminate recombination (so-called cage recombination), or conversely, the yield of free radicals undergoing so-called escape reactions, will in general depend on the initial spin multiplicity, the spin-independent probability of geminate re-encounters, the degree of spin evolution between successive re-encounters and hence on the average time elapsing between these and on the strength of an applied magnetic field. From the details of the magnetic-field dependence of the radical pair kinetics one can draw conclusions about the mechanism responsible for the spin evolution. In addition, rate parameters characteristic of the various reaction channels of the radical pair may be evaluated. The principles outlined above have been studied for many examples of radical pairs in homogeneous solutions, where the geminate re-encounter probability decays within several nanoseconds to tens of nanoseconds. In theses cases spin evolution is only probed during a correspondingly short interval of time. On the other hand, much longer periods of geminate re-encounters are found in micellar solutions where the micelles, with typical radii of about 20 Å, act as kind of supercages (4) for the radical pairs generated within them. When choosing microemulsion nanodroplets as media for studying magnetic-field dependent radical kinetics, it was our intention to take advantage of the polar interior of these aggregates for assisting electron transfer reactions and of the ease of size variation of the nanodroplets which can be extended much beyond the size of normal micelles, so that a wider range of time intervals between geminate re-encounters can be realized.

This allowed us to extend the study of radical pair spin evolution to longer times than previously accessible.

2. MAGNETIC FIELD EFFECTS WITH TRIPLET RADICAL PAIRS

In polar media triplet radical pairs may be conveniently generated by using photo electron transfer reactions with dye triplets. Various aspects of such reactions, especially the dependence of free radical yield on solvent polarity, solvent viscosity and specific properties of electron donors have been studied in our laboratory using thionine and related dyes as excited triplet electron acceptors (5-8). One of the main characteristics of our findings concerning the yield of free radicals and its magnetic-field dependence in homogeneous solutions was, that geminate recombination in radical pairs of the type $^3(A^{\cdot} \ D^{\cdot +})$ is only of minor importance. However, the yield of free radicals is significantly affected by heavy atom substituents, an effect which has been attributed to the enhancement of intersystem crossing (ISC) in a triplet exciplex $^3(AD)^+$ assumed to be a precursor of the solvent-shared radical pair. The lack of geminate radical pair effects in homogeneous solution must be attributed to the absence of Coulombic attraction in radical pairs of the 0/+ charge type, which renders geminate re-encounter probabilities too low, thus precluding radical pair spin evolution to become kinetically apparent.

The reverse micellar system including the w/o microemulsion region of w we utilized for the study of geminate radical pair recombination kinetics and spin effects was made up of cetyldimethylbenzylammonium chloride (CDBA) solutions (0.04 M) in benzene with various amounts w of water added, wherein the cationic dye had been dissolved. Dye concentrations were such that the average population of a nanodroplet was of the order of a few percent, so that production of more than one RP per nanodroplet was negligible. The H_2O/CDBA/benzene reverse micellar system was first introduced by Klein, Hauser and Miller (9). According to their results aggregation numbers increase approximately proportional to w^2 for w>10, a behaviour which is consistent with the nanodroplet model of microemulsions (1). In this region of w the nanodroplet radius varies approximately as 1.9 w Å.
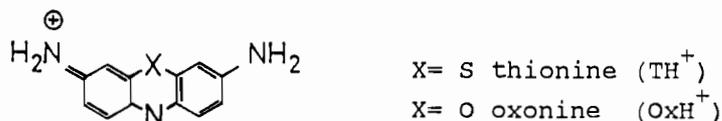
2.1 Radical pair kinetics in nanodroplets of variable size

The influence of nanodroplet size on geminate RP recombination kinetics and its magnetic-field dependence was studied in detail for RPs produced by quenching thionine triplet with aniline as electron donor (10). Although aniline is solvated mainly in the unpolar bulk phase its access to the dye triplets in the polar interior of the surfactant/water aggregates is not inconveniently reduced as compared to the kinetics in homogeneous solution. For w=15 the bimolecular quenching rate constant was found to be

$$H_2\overset{\oplus}{N}\diagup\!\!\diagdown X\diagdown\!\!\diagup NH_2 \qquad \begin{array}{l} X= S \text{ thionine } (TH^+) \\ X= O \text{ oxonine } (OxH^+) \end{array}$$

$1.4x10^9M^{-1}s^{-1}$, dropping to about $6x10^8M^{-1}s^{-1}$ for w=32.5, which is to be compared with a value of $3.4x10^9M^{-1}s^{-1}$ for methanolic solution. Thus, with an aniline concentration of 0.05 M triplet decay is fairly complete after 30 ns, even for the highest w applied. In the quenching process an electron is transferred from aniline to the dye triplet, giving rise to the typical dye semiquinone spectrum, which in the reverse micellar system resembles very much that in methanol. The kinetics of semithionine decay was followed by nanosecond laser flash spectroscopy using an excimer-laser-pumped dye laser for excitation. Characteristic signals observed with various values of w are shown in Figure 1. Kinetically the decay proceeds in two steps. The faster one, occuring in the 200 - 1000 ns time regime, is unparalleled in homogeneous solution and must be attributed to geminate intra-nanodroplet radical pair recombination, whereas the slower kinetic component which extends to the millisecond region, belongs to the non-correlated inter-nanodroplet radical recombination, corresponding to the homogeneous second order rate process observed in homogeneous solution. The quantitative kinetic analysis of the geminate process was based on the following kinetic scheme (I), according to which the dye radical concentration c_{TH}. decays as given in eq.[1]:

$$c_{TH}\cdot(t) =$$

$$c_{TH}\cdot(0)[k_{esc}/(k_{esc}+k_{rec})]\{1+(k_{rec}/k_{esc})\exp[-(k_{esc}+k_{rec})t]\} \quad [1]$$
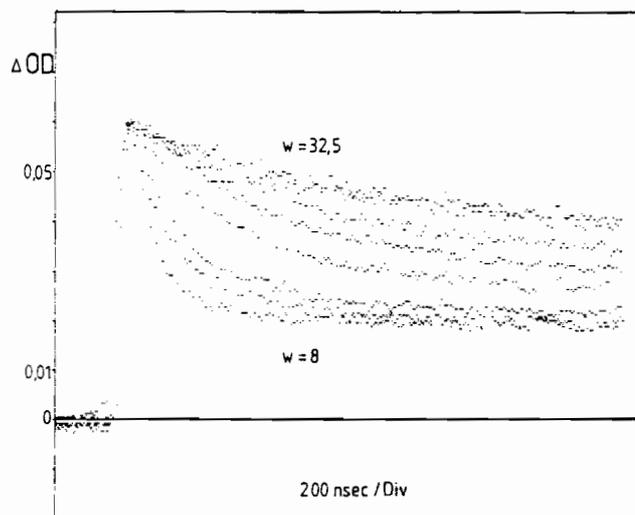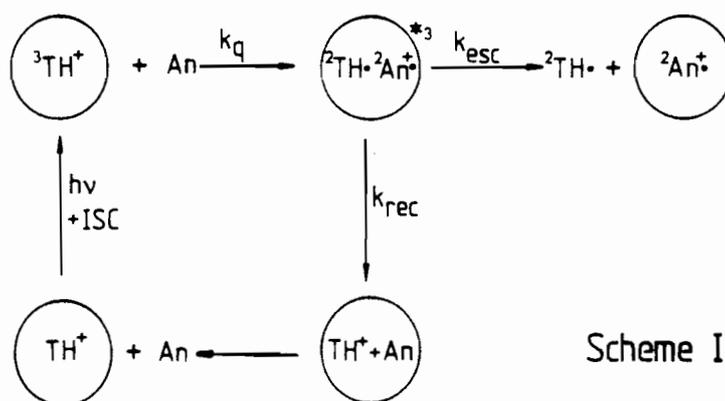
Fig.1. Radical pair recombination kinetics observed at zero field with RPs obtained from thionine triplet quenching by aniline in water/CDBA/benzene microemulsions of various w (8, 11.5, 15, 18.5, 22, 25, 5, 29, 32.5). The absorption of thionine semiquinone radical was monitored at 420 nm using the technique of laser flash spectroscopy (25).

Scheme I

Using the first-order rate constants k_{rec} for geminate recombination and k_{esc} for escape of a radical from the nanodroplet of its generation the efficiency of radical pair escape η_{esc} is given by

$$\eta_{esc} = k_{esc}/(k_{esc} + k_{rec}) \qquad [2]$$

The rate constants obtained for various w by applying kinetic fits based on eq.[1] to the observed radical decay curves are plotted versus w in the diagrams shown in Figure 2.

The values of k_{rec} are strongly w-dependent, varying approximately as w^{-3} for w>15, which implies an inverse proportionality to the volume of the nanodroplets, as would be expected for a diffusion-controlled process if the reactants were free to move in the volume of the intramicellar water core. Also indicated in the diagram are the lines to be expected theoretically for diffusion controlled pair reactions in homogeneous spheres with radii corresponding to those of the nanodroplets investigated and assuming a viscosity of 1 cP (like that in bulk water) or 10 cP, respectively. Since the observed values of k_{rec} are clearly lower, it is not very likely that the radical pairs undergo unrestricted motion in the water pool, unless the water there is assumed to have a much higher viscosity than free bulk water.
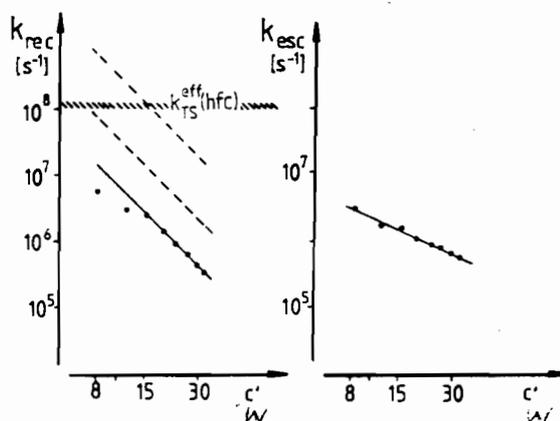

Fig.2. Rate constants k_{rec} and k_{esc} of Scheme I evaluated as a function of w from transient signals as shown in Figure 1.

Most probably the radicals will be associated with the Stern layer at the water/surfactant interface for most of the time, being only occasionally released for free diffusional trips into the interior of the water pool. Possibly these trips are the main transport mechanism by which geminate radical pair re-encounters are brought about.

Since the radical pairs are produced with triplet spin alignment they cannot recombine before having undergone a triplet-to-singlet spin change. In Figure 2a is also indicated the effective rate constant at which such processes should occur at zero magnetic field. This value of about $10^8 s^{-1}$ was derived from

the theory of spin motion as induced by isotropic hyperfine coupling (11,12) in the radical pairs considered here. Comparing this rate constant with the observed rate constant of radical pair recombination it becomes clear that in zero field the spin process cannot be the rate determining step of the recombination process. Under the prevailing conditions the radical pair should recombine as if in spin equilibrium, i.e. show no spin memory for the precursor multiplicity.

Compared to k_{rec} the w dependence of k_{esc} is much weaker and is approximately proportional to w^{-1}, i.e. to r_{nd}^{-1}. The r_{nd} dependence of k_{esc} is the same as that of the surface-to-volume ratio in a sphere and could be interpreted as indicating a uniform distribution of the escaping radical species over the nanodroplet volume. However, as pointed out above, this interpretation would be at variance with the low absolute value of k_{rec}.

Whereas for the reaction system considered in this section there is no indication of spin memory effects on the radical recombination kinetics at zero field, such effects become clearly apparent if magnetic fields are applied (cf. Figure 3). As the field becomes higher the geminate process is slowed down and the yield of escaping radicals is concomitantly increased. A kinetic analysis of the decay curves according to eq [1] showed that only the rate constant k_{rec} is significantly affected by a magnetic
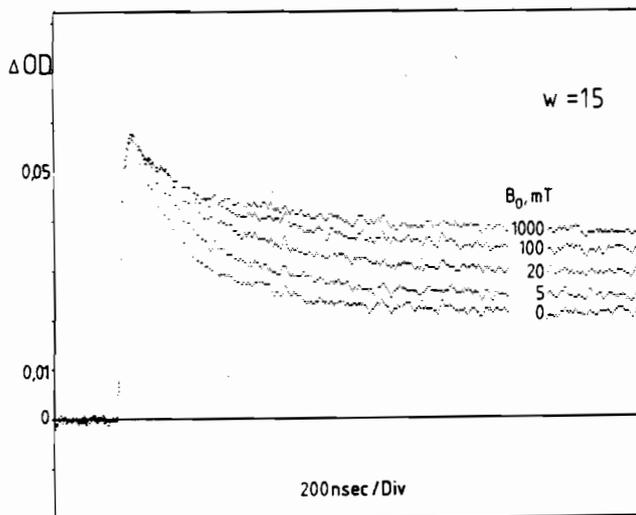

Fig.3. Magnetic-field dependence of transient kinetics with $^3(TH \cdot \ An \cdot^+)$ RPs in CDBA-enclosed water nanodroplets in benzene (adapted from ref 10). Conditions of observation as in Figure 1.
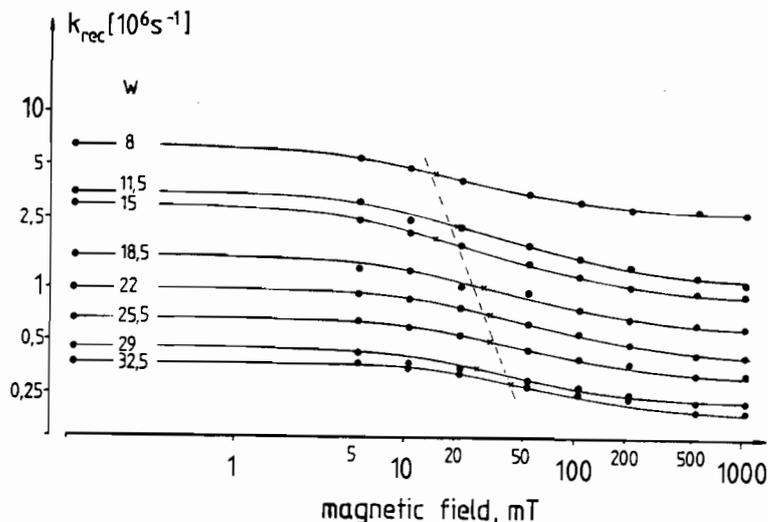
Fig.4   Magnetic-field dependence of rate constant k_{rec} of gemi-
nate recombination of ^{3}(TH· An·$^+$) RPs in water/CDBA/benzene
microemulsions for various w values corresponding to nanodroplet
radii between 15 Å and 60 Å (10).

field (10). Its field dependence in nanodroplets of various size
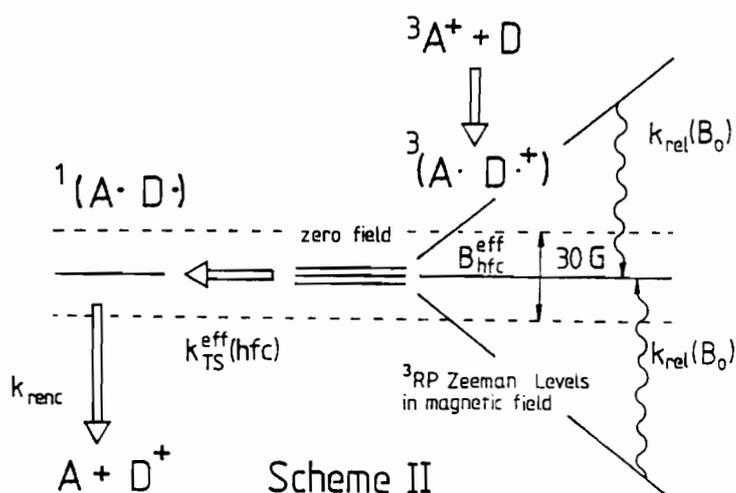is depicted in Figure 4.

Although the absolute values of k_{rec} vary by a factor of
about 20 over the range of w-variation, the shapes of the curves
representing the magnetic-field dependence are essentially
unchanged. The field dependence seems to approach saturation at
fields of about 1 Tesla, where k_{rec} is reduced by a factor of two
to three with respect to its corresponding zero-field values. On
each curve is marked the interpolated position where

$$k_{rec}(B_{1/2}) = k_{rec}(B=0 \text{ T}) + 0.5(k_{rec}(B=1 \text{ T}) - k_{rec}(B=0 \text{ T})) \qquad [3]$$

which defines a corresponding $B_{1/2}$ value for each w. Despite the
scatter displayed by these $B_{1/2}$ values, there is a clear trend
for $B_{1/2}$ to increase with the nanodroplet radius ($B_{1/2} \approx 14$ mT
for w = 8 to $B_{1/2} \approx 40$ mT for w = 32.5). The slope indicated
corresponds to a value of -2, implying a relation:

$$k_{rec}(B_{1/2}) \sim B_{1/2}^{-2} \qquad [4]$$

A qualitative explanation of the **magnetic** field dependence found

$$^3A^+ + D$$

$$\Downarrow$$

$$^3(A\cdot D\cdot^+)$$

$$^1(A\cdot D\cdot)$$

$$k_{rel}(B_0)$$

- - - - - - - zero field - - - - - -

$$B_{hfc}^{eff} \quad 30\,G$$

$$k_{TS}^{eff}(hfc)$$

$$^3RP\ Zeeman\ Levels$$
$$in\ magnetic\ field$$

$$k_{rel}(B_0)$$

$$k_{renc}$$

$$A + D^+ \qquad \text{Scheme II}$$

for k_{rec} can be given in terms of Scheme II. In order that a RP be able to recombine, its total electron spin has to acquire some singlet character. As explained above, this cannot be a rate determining process in zero field since $k_{TS}^{eff}(hfc) \gg k_{renc}$. However, as the field increases, the increase of the Zeeman splitting will slow down spin equilibration between the outer and central Zeeman levels and eventually render it sufficiently slow so that it may become apparent in the recombination rate constant. The facts that $B_{1/2}$ is several times larger than the effective isotropic hyperfine field of about 30 Gauss (3 mT) calculated by a relation given by Weller et al. (13), and that a definite saturation limit of the magnetokinetic effect is not attained below 1 T, clearly indicate that T-S coupling mechanisms other than isotropic hyperfine coupling (i.e. the one which is responsible for CIDNP and CIDEP effects) are still operating on the time scales of our experiments even at fields where this isotropic hfc mechanism of $T_\pm/T_o$,S mixing has been suppressed. These mechanisms must imply exchange of the $T_\pm/T_o$,S energy difference between the electron spin system and the bath, i.e. they must correspond to longitudinal magnetic (T_1-) relaxation processes. Only if these processes become slow enough (compared with the re-encounter rate characterized by a rate constant k_{renc}) a magnetic field effect will appear in the recombination kinetics. Thus we may assume that the magnetic-field dependence observed for k_{rec} reflects the magnetic-field dependence of the relaxation rate constant k_{rel}. As a consequence of this, however,

we have to infer from Figure 4 that k_{rel} must strongly depend on w, namely in the same way as $k_{rec}(B=0) \approx 1/4\ k_{renc}$. This would imply that electron spin relaxation in the radical pair occurs mainly during re-encounters. This is a strong indication that the dominant spin relaxation mechanism in question might be provided by the stochastic modulation of magnetic dipolar interaction between the two radical spins during a re-encounter. Estimates of the contribution of such a mechanism have been reported by Hayashi and Nagakura (14). Their results show a strong field-dependent decrease of the corresponding relaxation rate constant which is also of the appropriate order of magnitude. To see in which way the w-dependence of $B_{1/2}$ observed in our investigation can be related to this mechanism will, however, require a more detailed quantitative treatment.

2.2   Spin-orbit coupling effects on magnetokinetic behaviour of triplet RPs.

In low viscosity homogeneous solvents spin motion has no appreciable effect on the efficiency of geminate recombination for RPs of the type $^3(A^{\cdot}\ D^{\cdot +})$, because the probability of geminate re-encounters is too small Nevertheless a very marked decrease of the free radical yield has been observed even in homogeneous solutions of low viscosity, on introducing heavy atom substituents into the electron donor (15). These effects and their magnetic-field dependence have been quantitatively accounted for by considering spin-orbit coupling in the triplet exciplex preceding the formation of a solvent-shared radical pair (16). Using microemulsion nanodroplets as a reaction medium the long periods during which geminate re-encounters take place in such aggregates made it possible to study the role of spin-orbit coupling on the spin evolution in radical pairs,too.

The data presented in Table 1 characterize radical formation and geminate recombination kinetics in several systems involving thionine triplet quenching by halogen anilines. Two main effects are borne out by the free radical yields. As in methanol, in the reverse micellar system too, the free radical yield decreases monotonically with increasing spin-orbit coupling (note the position-dependent effect of the bromine substituent, which may be also related to the effect of spin-orbit coupling, since the latter depends on the density of the unpaired electron experienced by the heavy atom nucleus in the oxidized donor radical (6)). Comparing the same donor in both solvents, the free radical yield

TABLE 1

Radical production and geminate RP decay with halogen anilines as quenchers of thionine triplet in MeOH and reverse micelles

electron donor	MeOH[a)] Φ_{fr}[c)]	CDBA reverse micellar system (w = 15)[b)]				
		Φ_{fr}[c)]	η_{esc}[d)]	k_{esc}[e)]	k_{rec}[e)]	f_{rec}[f)]
aniline	1.00	0.29	0.36	1.75	3.0	3.2
4-Cl	0.97	0.27	0.40	1.75	3.0	1.9
3-Br	0.90	0.21	0.48	2.9	3.1	1.5
2-Br	0.70	0.13	–	–	–	–
4-Br	0.51	0.10	0.45	2.9	3.4	1.0
4-I	0.13	0.06	0.38	3.1	5.1	1.0

[a)] from ref 17 [b)] from ref 18 [c)] yield of free radicals for complete triplet quenching [d)] cf. eq.[2] [e)] in units of $10^6 s^{-1}$ [f)] defined as $k_{rec}(B=1T)/k_{rec}(B=0T)$

is reduced in the micellar system by a factor of 2 - 5. Nanosecond time-resolved experiments have shown that in all of these systems a considerable fraction of radicals , present immediately after the triplet quenching, decays in a geminate process on the nanosecond time scale (18,25). The rate constants of geminate radical pair decay are not very sensitive to heavy atom substitution. With the help of the time-resolved measurements the yield of free radicals Φ_{fr} may be decomposed into a product of the initial yield of RPs Φ_{rp} which depends on SOC according to the exciplex mechanism and a factor η_{esc} measuring the efficiency of radical escape, which is practically 1 in homogeneous methanolic solution and between 0.36 and 0.48 in the reverse micellar system (eq [5]). In zero field the factor η_{esc} is not significantly modified by heavy atom substitution. This again emphasizes that in zero field spin evolution does not seem to be the rate determining step in geminate recombination of triplet RPs produced in such reverse micellar aggregates.

$$\Phi_{fr} = \Phi_{rp} \cdot \eta_{esc} \qquad [5]$$

The relative magnetic change of the free radical yield in the CDBA reverse micellar system was recorded as a continuous function of a magnetic field (18) with the donors listed in TABLE 1. These so-called MARY (19) spectra are displayed in Figure 5.
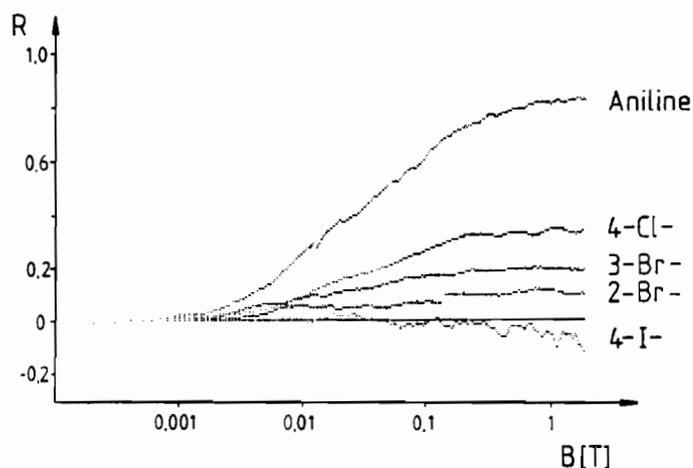
Fig.5 MARY spectra of relative magnetic field effect R on the free radical yield resulting from thionine triplet quenching by various halogen anilines in water/CDBA/benzene microemulsions. The yield of free radicals was monitored by thionine ground state depletion at 610 nm 20 μs after the laser pulse (18).

For the systems with 4-Cl-, 3-Br- and 2-Br-aniline they have practically the same shape and the same $B_{1/2}$ as observed with aniline. However, the MARY intensity is reduced as the spin-orbit coupling increases. Again, there is the 3- > 2- > 4-position dependence of the substituent SOC effect. For the 4-Br-aniline the MARY intensity is zero and not depicted in Figure 5. For the 4-I-derivative the MARY spectrum shows a negative intensity, however with a significantly higher $B_{1/2}$ than in the other cases.

Nanosecond time-resolved magnetokinetic experiments have re-vealed that the positive MARY intensity in Figure 5 is due to a magnetic-field dependence of k_{rec} which renders η_{esc} magnetic field dependent (18,26). However, due to the heavy atom substi-tuents, the geminate radical pair recombination process becomes less susceptible to a magnetic field. This means that the rate of triplet-singlet transitions which is slowed down in a magnetic field, is less strongly affected if heavy atoms are present. We suggest that this may be due to an increasing contribution of the spin-rotational relaxation mechanism, which is independent of the

$$k_{rel}(s\text{-rot}) = 1/T_1 = (12\pi r^3)(\Delta g_\parallel{}^2 + 2\Delta g_\perp{}^2)kT/\eta \qquad [6]$$

magnetic field strength and increases with the square of the g-tensor anisotropy, which relates it directly to the strength of

spin-orbit coupling (20). Making use of the relation in eq [6], where r is the hydrodynamic radius of the radical (here we assume a value of 3 Å) and η is the viscosity of the solvent, we expect the following values (18):

4-Cl: $2 \times 10^5 \eta^{-1}$ s^{-1}cP   3-Br: $7 \times 10^5 \eta^{-1}$ s^{-1}cP

4-Br: $3 \times 10^6 \eta^{-1}$ s^{-1}cP   4-I : $1 \times 10^7 \eta^{-1}$ s^{-1}cP

These rate constants will mark the lower limits to which the $T_{\pm} \rightarrow$ S,T_O relaxation rate constant may be decreased by a magnetic field. If $k_{rel}(B \rightarrow \infty) > k_{rec}(B=0)$ no magnetic field effect will be found. If $k_{rel}(B \rightarrow \infty) < k_{rec}(B=0)$ and approaches $k_{rec}(B=0)$ from below, as in the donor series investigated, the saturation value of the magnetic-field effect will go down. Under the conditions at which the MARY spectra in Figure 5 were obtained $k_{rec}(B=0) \approx 3 \times 10^6 s^{-1}$. Setting η = 1 cP (the viscosity of bulk water) the k_{rel}(s-rot) values in the substituent series listed above would in fact approach and exceed $k_{rec}(B=0)$ which can explain the observed reduction and finally complete disappearance of MARY intensity with these substituents. It must be pointed out, however, that the results on the w-dependence of $k_{rec}(B=0)$, as described in the last section, suggest a significantly higher effective viscosity for the <u>translational</u> motion of the radicals.

As for the negative sign of the MARY effect with 4-I-aniline, we suppose that this is due to a magnetic-field effect on Φ_{rp} and is caused by the triplet mechanism, which is also found in homogeneous solution. The corresponding effects to be expected for the other halogen derivatives investigated here are much smaller, so that they are not detectable at the level of experimental accuracy available with the low dye concentrations in the micellar systems.

3.   MAGNETIC FIELD EFFECTS WITH SINGLET RADICAL PAIRS

Since radical pairs produced with singlet spin alignment may undergo spin-allowed fast recombination to form singlet ground state products the yield of detectable, freely diffusing radicals is usally very low when singlet precursors are involved. Exceptions may be found where the singlet recombination becomes slow due to unfavourable Franck-Condon factors, which requires that the energy of the radical pair is fairly high (typically > 20000

cm^{-1}) In such cases recombination to form a locally excited triplet state may be faster if the radical pair has achieved the necessary triplet spin alignment (21,22). Another type of cases where high radical yields ensue form electron transfer reactions with an excited singlet state has been encountered by Iwa et al.(23) with singlet excited oxonine/electron-rich aromatic amine donor systems. Here the radical pair energy is far below the excited singlet state and, in fact, is already closely above the singlet ground state of the pair of reactants. Due to the chemical similarity of such a singlet reaction system with our systems for generating the triplet radical pairs, we chose the reaction between oxonine singlet and N.N-tetramethylparaphenylene diamine (TMPDA) showing a Φ_{fr} or 0.48 in methanolic solution, to investigate the magnetic-field dependent reaction kinetics of radical pairs generated with <u>antiparallel</u> spins in microemulsion nanodroplets.

Oxonine (OxH^+) and its semireduced radical ($OxH^{\cdot}$) have absorption spectra which closely resemble the corresponding ones of thionine and its semiquinone radical. Due to the replacement of the S-atom in thionine by the lighter O-atom in oxonine the spin-orbit coupling is reduced to an extent that practically no spontaneous triplet formation occurs, so that no triplet reaction will interfere and the spin alignment of the generated radicals corresponds to a well defined singlet. In the CDBA reverse micellar system photoexcited oxonine produced an appreciable background of long-lived transient absorption. Therefore the investigations were carried out in microemulsions made up of H_2O/AOT nanodroplets in isooctane. This system is very well known in the literature. The relation between the radius of the surfactant-coated nanodroplets and the water/surfactant ratio w has been experimentally determined by the method of dynamic light scattering (1). Using this method it was also confirmed by Eicke and coworkers (24) that TMPDA concentrations up to 0.1 M in the oil phase do not cause significant changes of the radii of the nanodroplets.

As in homogeneous methanolic solutions, in the AOT reverse micellar system, too, a considerable amount of $OxH^{\cdot}$ radicals are detectable after a laser flash, when $^1OxH^{+*}$ is quenched by TMPDA (26,27). The kinetic behaviour of the radicals as observed on the nanosecond time scale is shown in Figure 6 for various w and for a homogeneous solution in methanol. At the particular wavelength
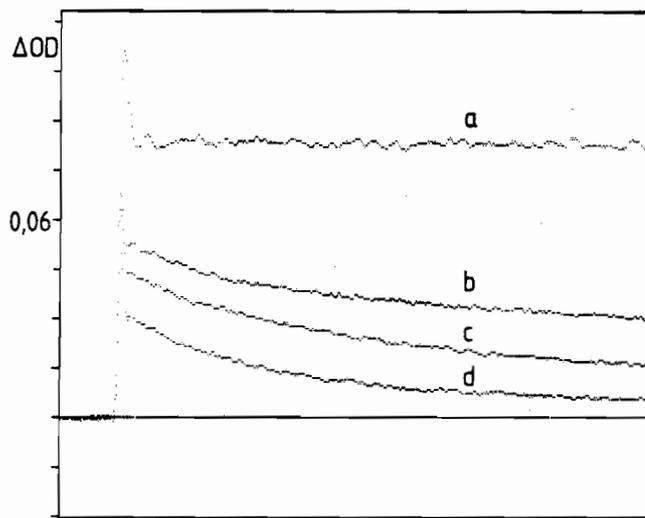
Fig.6 RP recombination kinetics observed at zero field in water/AOT/isooctane microemulsion (w= 32 (b), 16 (c), 8 (d)) and in methanol (a) with RPs resulting from 70% quenching of oxonine fluorescence by TMPDA (27). The oxonine semiquinone radical was monitored at 413 nm. The time scale is 100 ns/div for (a) and 200 ns/div for (b-d).

where the radical kinetics is recorded there is also an appreciable $S_1 \rightarrow S_n$ absorption of the dye, causing a pronounced absorption peak during the laser flash. Two main features are documented by Figure 6. Firstly, the amount of radicals detectable directly after the laser increases with w and is largest in pure methanol. Since care was taken that the same amount of laser quanta were absorbed in each experiment and the degree of fluorescence quenching, as controlled by the TMPDA concentration was the same, this result implies that there is a certain amount of very rapid geminate RP recombination taking place already during the laser excitation, the contribution of which decreases with w and has the least effect in the homogeneous solvent. Secondly, the radical decay in the microemulsion system is almost entirely geminate, whereas the radical decay in methanol extends to the millisecond region and is of second order with a rate constant of $2.8 \times 10^9 s^{-1}$. As was also found in the case of thionine/aniline RPs in CDBA based microemulsions, the rate constant of recombination to be followed on the time scale of several hundred nanoseconds decreases with w. However, the w-dependence of k_{rec}, which in the present system may be approxima-
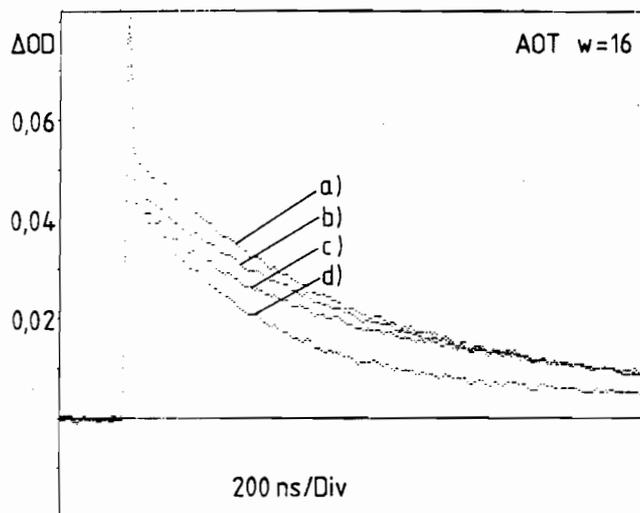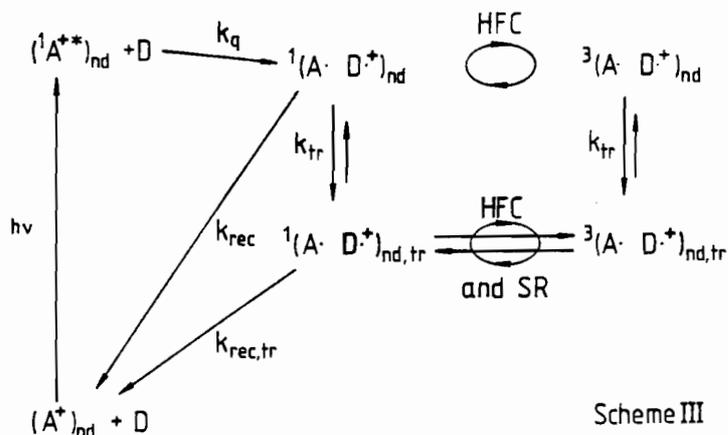
Fig.7 Magnetic-field dependence of singlet RP kinetics (26). Conditions correspond to those described in Figure 6, curve c.

ted by a proportionality to w^{-1}, is much less pronounced than in the former case. The magnetic field effect on the radical pair recombination kinetics is shown in Figure 7. Whereas there is only a very small decrease ($\approx 2\%$) of the free radical yield in methanol, in the microemulsion system the corresponding change in the amount of radicals present directly after the laser flash is about -20%. The magnetic-field effect in the microemulsion system is a twofold one. Besides the decrease of the amount of radicals detectable at the earliest times after the laser pulse, the magnetic field effect on which shows a $B_{1/2}$ of about 8 mT and saturates below 50 mT, there is also a magnetic-field effect on the geminate recombination kinetics. The effective first order rate constant k_{rec} of geminate recombination remains fairly constant up to fields of the order of 50 mT but then increases by a factor of 1.8 when the field is raised to 1 T.

An interpretation of the observed kinetic behaviour and its magnetic field dependence can be given in terms of Scheme III, according to which two different types of RPs have to be considered. One of them recombines on a time scale shorter than 10 ns, the other one on the time scale of several hundrerd nanoseconds. The species related to the latter process will be denoted as 'trapped' radical pair, whereby it is implied that both radicals are immobilized in the waterpool/surfactant inter-

$$(^1A^{+*})_{nd} + D \xrightarrow{\ k_q\ } {}^1(A^{\cdot}\ D^{\cdot +})_{nd} \qquad \overset{\text{HFC}}{\bigcirc} \qquad {}^3(A^{\cdot}\ D^{\cdot +})_{nd}$$

$$k_{tr} \quad\quad\quad k_{tr}$$

$$h\nu \qquad k_{rec} \quad {}^1(A^{\cdot}\ D^{\cdot +})_{nd,tr} \overset{\text{HFC}}{\underset{\text{and SR}}{\rightleftharpoons}} {}^3(A^{\cdot}\ D^{\cdot +})_{nd,tr}$$

$$k_{rec,tr}$$

$$(A^{+})_{nd} + D \qquad\qquad \text{Scheme III}$$

face layer, whereas in the other type of RP at least one of the radicals may be able to diffuse freely through the water pool until it recombines with its geminate counterpart or it becomes trapped, too. That there must be two types of RPs with largely different mobilities has already been inferred from the w-dependence of the radical concentration after the laser flash. The fact that the initial yield of this more slowly recombining type of RP may be influenced by a magnetic field leads us to assume the possibility of conversion of the fast-diffusing type of RP into the trapped one. Although it cannot be excluded that part of the trapped RPs originate directly in this situation through the photoelectron transfer process, a considerable part of them must originate as the freely diffusing RP type. With this assumption the magnetic field effect on the yield of trapped RPs can be explained as a consequence of spin evolution in the fast-diffusing RP. This spin evolution, which during the few nanoseconds of the lifetime of the latter type of RP can be brought about only by the <u>coherent</u> hfc mechanism, decreases the initial singlet character of the RP, thus decreasing also its recombination probability. However, the coherent $S \rightarrow T_{\pm}$ mixing process may be suppressed by quite small magnetic fields, so that the singlet character tends to be preserved for a longer time and the recombination will occur more efficiently in a magnetic field, with a concomitant decrease of trapped radicals. In fact a model calculation based on this mechanism allowed us to estimate the values of the rate constants k_{rec} ($\approx 10^9 s^{-1}$) and k_{tr} ($\approx 10^8 s^{-1}$) from the magnetic field dependence of the yield of trapped radicals (26).

When the RPs are in the trapped situation re-encounters occur
much less frequently and there is enough time for spin equilibra-
tion, even in fields where the coherent $S \rightarrow T_\pm$ process is already
suppressed. In order that the corresponding <u>incoherent</u> process be
also slowed down below the re-encounter frequency, higher fields
are necessary. If this requirement is met the recombination rate
constant will increase. Assuming that on each re-encounter in
zero field the trapped RPs recombine with a probability of 25%,
corresponding to a spin-statistical singlet character, and in
high field, where only $S \rightarrow T_o$ equilibrium can be established
between two re-encounters, with a probability corresponding to a
50% singlet character, a maximum magnetokinetic effect of +100%
on $k_{rec,tr}$ may be anticipated. In fact, the observed increase in
$k_{rec,tr}$ of +80% at 1 T is quite close to this theoretical limit.

4.   CONCLUSION

In this contribution we have summarized and discussed the
results of our investigations on several basic aspects concerning
the behaviour of spin-correlated radical pairs enclosed in the
nanodroplets of w/o microemulsions.

The recombination kinetics of radical pairs created with
<u>triplet spin correlation</u> was systematically studied as a func-
tion of nanodroplet size and magnetic field. The time constants
of recombination varied from 0.15 μs to 2.6 μs. They were
proportional to the volume of the water nanodroplets, however
the recombination was clearly slower than to be expected for a
diffusion-controlled process in the interior of the nanodroplets.
In zero magnetic field the decay of spin correlation due to
isotropic hyperfine coupling is faster than the re-encounter
process and not rate determining for recombination. In a magnetic
field of 1 T the effective recombination rate constant is slowed
down by a factor of 2 - 3. The field $B_{1/2}$ necessary to obtain
half of the 1 Tesla effect increases from 14 mT to 40 mT as a
monotonic function of the nanodroplet radius. The magnetic-field
dependent recombination rate reflects the magnetic-field depen-
dence of a spin relaxation process which depends on radical pair
re-encounters and may be attributed to electron spin dipolar
interaction. Application of halogen substituted radicals revealed
contributions of a magnetic-field independent spin relaxation
mechanism, the importance of which gradually increases with the

spin-orbit coupling in the corresponding radical. This effect is most probably due to the spin-rotational relaxation mechanism.

When creating radical pairs with <u>singlet spin correlation</u> radical recombination processes and magnetic-field effects could be separately observed in two different time and field domains (≤ 10 ns, ≤ 50 mT; ≥ 100 ns, ≥ 50 mT). They may be attributed to radical pairs diffusing freely through the interior of the water nanodroplet and others which are immobilized in the water/surfactant interface. A magnetic field accelerates the recombination due to interference with the (coherent) isotropic hyperfine coupling mechanism in the first case and with (incoherent) relaxation mechanisms in the second case.

In concluding we note that future developments in the application of magnetokinetic effects to micellar and microemulsion systems will need to develop quantitative models of spin relaxation. These will then provide access to specific details of radical pair motion in such media and thus will add to the basic knowledge which is required for a systematic progress in the methods of reaction control.

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