

MAGNETIC-FIELD-ENHANCED RADICAL YIELD FROM TRIPLET ELECTRON-TRANSFER REACTION IN REVERSED MICELLES

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The radical yield in the electron-transfer reaction between thionine triplet and aniline in reversed micelles is increased by an external magnetic field. The saturation value of the effect amounts to 85% (18 kG) and the $B_{1/2}$ value is 300 G. The magnetic-field effect is discussed on the basis of the radical-pair mechanism with a quantitative consideration of the hyperfine-induced spin motion.

1. Introduction

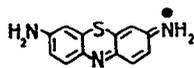
Micellar solutions as reaction media have been attracting the interest of chemists and photochemists for quite a while [1,2]. In a sense micelles act as large solvent cages which may cause drastic enhancements of isotope and magnetic-field effects in reactions involving radical pairs [3]. In micellar systems time-resolved geminate pair kinetics, which in homogeneous solution has been observed on a time scale of a few nanoseconds [4,5], has been found to be extended to a period of almost one microsecond by the groups of Hayashi [6–8], Turro [9], Scaiano [10,11] and Tanimoto [12,13]. These reports refer to triplet radical pairs produced from aromatic ketones either by α -cleavage or by H-atom transfer from some H donor or the detergent itself. Geminate recombination is possible only after intersystem crossing (ISC) to the radical-pair singlet. Triplet–singlet transitions are induced by hyperfine (hf) interaction, and can be modified by external magnetic fields and isotope exchange. Recently Tanimoto et al. [14] reported a magnetic field effect in SDS–micellar solution, where the radical pair was produced by electron transfer. The effect amounting only to 5% was too weak, however, to be quantitatively analyzed.

In this paper we report our observation of a drastic magnetic-field effect, increasing the yield of radicals produced by electron transfer from aniline to thionine triplet in reversed micelles. In homogeneous solutions there is no magnetic-field effect detectable with this donor–acceptor pair, since the geminate pair time period is too short to allow for efficient hf-induced recombination. Only with heavy-atom substituted anilines magnetic-field effects occur which, however, are due to the triplet mechanism in triplet exciplexes [15, 16], preceding the radicals.

Since thionine is a cationic dye, micelles with polar interior are required for its solubilization which can be achieved by use of a reversed micellar system where the bulk phase is a hydrophobic solvent and the interior of the micelle is made up of water. Such reversed micellar systems have found considerable interest due to their potential biological model character (cf. refs. [17,18]). Our results represent the first magnetic-field effect reported for such a medium.

2. Experimental

Materials. Thionine (Merck) was purified according

Thionine, TH⁺

to ref. [19]. Aniline (Merck, p.A.) was distilled under vacuum. Cetyldimethylbenzylammonium chlorid (CDBA) (Fluka, purum) was used without further purification. Solutions of CDBA in benzene (Merck, zur Rückstandsanalyse) were 0.04 M. The dye was solubilized by adding a suitable amount of aqueous dye stock solution. The water used was deionized and doubly distilled in a quartz apparatus. In the solutions investigated the molar ratio of H₂O to CDBA was 13.5. The total dye concentration was $(5-6) \times 10^{-6}$. Before the laser flash investigations the solutions were flushed with N₂ (O₂ content less than 5 ppm) for 30 min.

Apparatus. The laser flash experiments were performed on the microprocessor-controlled dye laser flash spectrometer described previously [16]. The time resolution was determined by the laser pulse duration of 0.8 μ s.

3. Results and discussion

With the detergent and water concentrations used in our experiments the aggregation number of the micelles has been determined to be ≈ 150 [20], corresponding to a micelle concentration of 2.7×10^{-4} M. Thus one micelle contains ≈ 2000 molecules of water, whereas the mean occupation number of micelles by dye molecules is 2%. Under such conditions the absorption spectrum observed is very similar to that of dilute aqueous or methanolic solutions.

On flashing micellar solutions of thionine an intermediate spectrum with a lifetime of $\approx 100 \mu$ s is observed which closely matches the well-known triplet spectrum in homogeneous solutions. The maxima are found at 795, 720 and 425 nm.

Solutions of aniline in the micellar solution show the same absorption spectra as in pure benzene. The distribution coefficient of aniline between benzene and water has been determined as ≈ 10 at room temperature. If we treat the water pools in the micelles as a pure water phase, we obtain from the distribution coefficient and the volume ratio, that 0.1% of the aniline molecules should reside in the water pools. Thus it appears extremely improbable that an appreciable

fraction of thionine triplets is produced in micelles containing a donor molecule if the donor concentration is less than 10^{-3} M. Thus any reaction between thionine triplets and aniline requires diffusion of the donor molecules from the bulk benzene phase to the polar interior of the micelles where the cationic dye molecules must be located.

In the presence of aniline the triplet lifetime of TH⁺ is shortened. The quenching shows Stern-Volmer behaviour with a rate constant of $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Up to aniline concentrations of 10^{-3} M fluorescence quenching and quasi-static triplet quenching is negligible. In fig. 1 are shown transient signals observed at

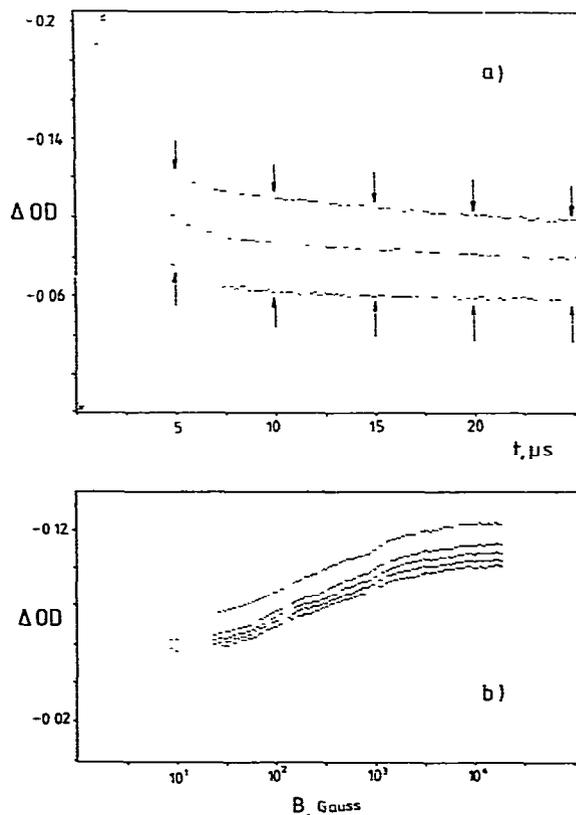
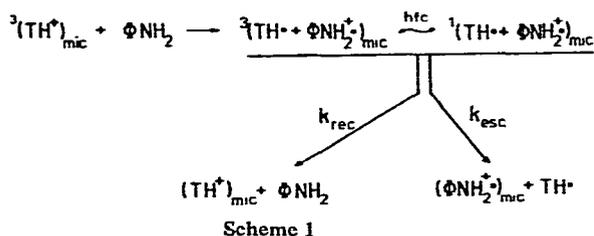


Fig. 1. (a) Transient signals observed at 610 nm on laser excitation of a micellar solution of TH⁺ (6×10^{-6} M) in the presence of 5×10^{-4} M aniline with magnetic fields (order from below) of 0, 300, 1000 G. (b) Magnetic field dependence of ΔOD at delay times of 5, 10, 15, 20, 25 μ s (order from top). The magnetic field was scanned continuously over 480 pulses; each data point represents an average of 30 pulses.

610 nm, the wavelength where ground-state depopulation is observed.

The fast decay in fig. 1 corresponds to the quenching of the triplet, repopulating the ground state, the slow decay is due to ground-state repopulation from the dye semiquinone radical. From the optical densities compared directly after the laser pulse and after 10 μ s when the triplet has been quenched, it follows that only $\approx 30\%$ of the triplets originally produced are converted to long-lived radicals in the quenching process. This is in contrast to observations in homogeneous solutions where in the same reaction almost 100% radicals can be observed in the microsecond region. The behaviour specific for micellar solution may be explained on the basis of scheme 1.



Dye triplets produced in the micelles ${}^3(\text{TH}^+)_{\text{mic}}$ are quenched by aniline diffusing into the micelle from the bulk phase during the lifetime of the triplet, and quenching is due to electron transfer producing a radical pair with triplet spin alignment in the water pool of the micelle. Geminate recombination will be possible as the radical pair acquires singlet character by means of the hf interaction. This recombination process will compete with the escape of one of the radicals (very likely the neutral radical TH $^{\cdot}$) into the bulk phase. Escape and recombination reaction are probably completed in less than 1 μ s [10,13] and not observable with the time resolution and the quencher concentration of the present experimental conditions. Thus, what is observed after the triplet has decayed, is the fraction of radicals that has escaped the micelle.

In the presence of an external magnetic field the transient signals change as shown in fig. 1. One observes a drastic increase in the yield of free radicals. In fig. 1b the magnetic-field effect is recorded at several delay times as a continuous function of the magnetic field, which is achieved by a special operating mode of the spectrometer [16]. The field dependence saturates at high fields and shows a $B_{1/2}$ value of 300

G. The maximum field effect, which has completely developed only after complete decay of the triplet (fig. 1b second trace from top) adopts a value of 85% at 18 kG.

A qualitative explanation for the magnetic field effect observed is provided by the hfc mechanism according to scheme 1. In an external magnetic field the Zeeman splitting of the triplet levels of the radical pair suppresses the hf-induced ISC to the singlet with a concomitant decrease of the geminate recombination rate constant. Since the escape process is not likely to be magnetic-field sensitive, the escape yield given by

$$\phi_{\text{esc}} = k_{\text{esc}} / (k_{\text{esc}} + k_{\text{rec}}) \quad (1)$$

must increase with the magnetic field. Assuming k_{esc} as magnetic-field independent, we have evaluated the function

$$n_{\text{rec}} = k_{\text{rec}} / k_{\text{esc}} = (1 - \phi_{\text{esc}}) / \phi_{\text{esc}}, \quad (2)$$

which is then proportional to k_{rec} . The magnetic-field dependence of n_{rec} is displayed in fig. 2 together with the magnetic-field effect R on the radical yield defined as

$$R(B) = [\phi_{\text{esc}}(B) - \phi_{\text{esc}}(0)] / \phi_{\text{esc}}(0). \quad (3)$$

In fig. 2 there are also shown the magnetic field effects observed by Scaiano and Abuin [11] on the escape fraction of radicals produced in the H-transfer reaction between 1,4-cyclohexadiene and benzophenone triplet in SDS aqueous micellar solutions and the "effective ISC rate constant" (cf. our discussion below) observed by Tanimoto et al. [13] for the radical pair anthrasemiquinone/SDS. In view of the different chemical nature of the systems compared, the similarity of the magnetic-field dependence is most striking and seems to reflect a general property of micellar systems.

Now we discuss the physical significance of the effective rate constant of recombination, k_{rec} , which in our opinion should not be identified with the rate constant " k_{ISC} " of the hf-induced ISC, as was generally assumed by previous workers reporting on magnetic-field effects in micelles [6-13]. In fig. 3 are shown the curves representing the development of singlet character in the triplet radical pairs pertinent to this work. The calculations are based on the semi-classical theory of Schulten and co-workers [21,22] which, though developed for singlet/triplet (S/T) ISC, can

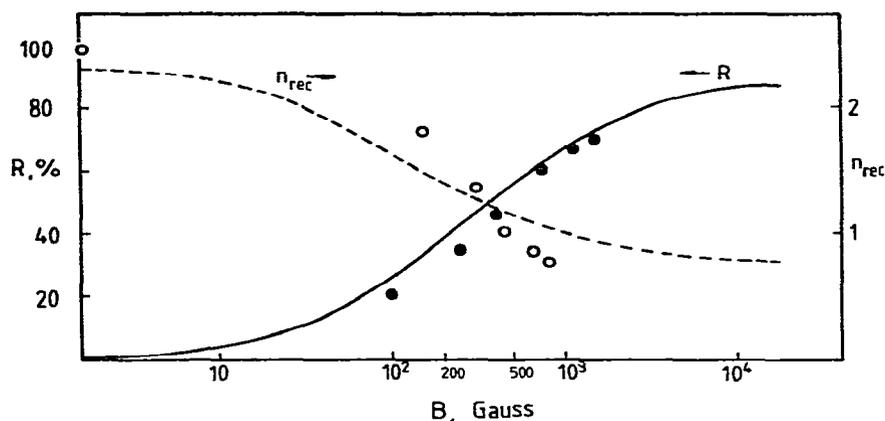
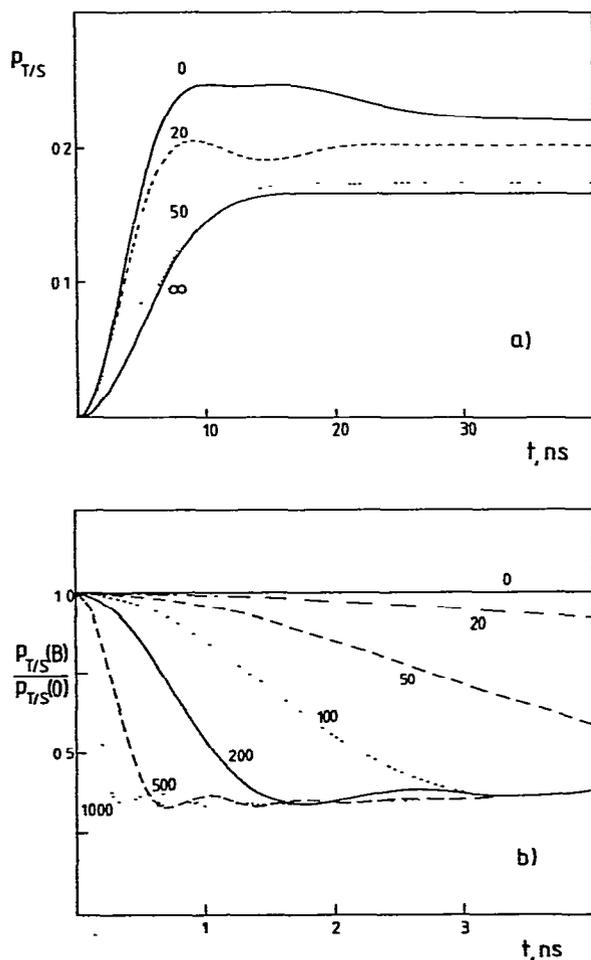


Fig. 2. Relative magnetic-field effect R on radical yield (solid line this work, \bullet from ref. [10]) and geminate radical-pair recombination rate constant (dashed line n_{rec} , this work, \circ $k_{\text{ISC}} \times 10^9$ s from ref. [13]).



easily be adapted to the T/S case using the relation

$$p_{\text{T/S}} = \frac{1}{3} p_{\text{S/T}} \quad (4)$$

The hyperfine coupling constants used were [23] (in gauss):

$$\text{TH}^{\cdot} \quad (1 \times a_{\text{N}} = 7.3, 2 \times a_{\text{H}} = 2.4, 2 \times a_{\text{H}} = 1.4),$$

$$\phi\text{NH}_2^{\cdot} \quad (1 \times a_{\text{N}} = 8.0, 2 \times a_{\text{H}} = 8.6, 2 \times a_{\text{H}} = 4.9,$$

$$2 \times a_{\text{H}} = 1.2, 1 \times a_{\text{H}} = 7.5).$$

From fig. 3a we note that a quasi-equilibrium value of $p_{\text{T/S}}$ is achieved after ≈ 10 ns. For radical pairs involving SDS radicals with stronger hfc [7] than in our radicals, this time constant would be even faster. It was found that " k_{ISC} " was in the range $(1-5) \times 10^6 \text{ s}^{-1}$ [11,12]. The identification

$$k_{\text{rec}} = k_{\text{ISC}} \quad (5)$$

must be rejected due to the following arguments:

(i) The development of singlet character due to hfc is not a stochastic process with a time-independent rate constant but rather a coherent spin motion where the effective first-order rate constant depends also on other processes probing the spin motion.

◀ Fig. 3. (a) Evolution of singlet character $p_{\text{T/S}}$ in the radical pair $^3(\text{TH} \cdot \phi\text{NH}_2^{\cdot})$ at different magnetic fields (values in G), calculated according to refs. [21,22]. (b) Details of the evolution of $p_{\text{T/S}}(B)$ at $t < 4$ ns, displayed relative to the zero-field function $p_{\text{T/S}}(0)$.

(ii) ISC due to hfc is not independent of the recombination reaction. If the distance of the radical pair is suitable for reaction the exchange interaction and the lifetime uncertainty broadening due to the reaction will suppress the spin motion [4].

Thus, instead of considering the hf-assisted pair recombination as a sequence of two independent rate processes where the first (slow one) is rate determining, one should rather describe it as a combined process with an effective rate constant according to

$$k_{\text{rec}} = k_{\text{diff,mic}} \bar{p}_{\text{T/S}}, \quad (6)$$

i.e. we assume that if the radical pair is in the singlet state recombination will be diffusion-controlled (note that $k_{\text{diff,mic}}$ is a first-order rate constant). The rate constant will be correspondingly smaller if the singlet character is less than one. By $\bar{p}_{\text{T/S}}$ we designate an average singlet character which depends on the average time interval which has elapsed since the radical pair had its last encounter and hence lost its singlet character due to reaction.

Encounters of radical pairs within a micelle may be described by an effective first-order rate process. The effective rate constant $k_{\text{diff,mic}}$ may be estimated by diffusion theory according to [24]

$$k_{\text{diff,mic}} = k_{\text{diff}} c_{\text{B}}, \quad (7)$$

where k_{diff} is the hypothetical second-order rate constant for the corresponding bulk medium and c_{B} is an effective concentration, corresponding to one molecule per volume of the micelle. Assuming that both radicals move freely in the water pool and that the viscosity is the same as in bulk water, we obtain $k_{\text{diff,mic}} = 2 \times 10^8 \text{ s}^{-1}$. Noting that

$$\tau_{\text{diff,mic}} = 1/k_{\text{diff,mic}} \quad (8)$$

can be regarded as the average time between two diffusive encounters of the radical pair, we see from fig. 3a that if $k_{\text{diff,mic}}$ is smaller than $\approx 5 \times 10^7 \text{ s}^{-1}$ corresponding to $\tau_{\text{diff,mic}} > 20 \text{ ns}$ $\bar{p}_{\text{T/S}}$ would approach 2/9 at zero field and 1/6 at high field, i.e. a maximum effect of 4/3 would ensue with a $B_{1/2}$ value of 25 G which is close to the value of 30 G obtained using a relation recently published by Weller et al. [25]. If, however,

$$k_{\text{diff,mic}} < \left(\frac{1}{6} \sum a_i^2 I_i(I_i + 1) \right)^{1/2} \\ = 1.5 \times 10^8 \text{ s}^{-1} \quad (9)$$

(the square-root expression contains the sum over the hfc constants a_i and spin quantum numbers I_i of all the relevant magnetic nuclei in the radical pair [21,22]) the ratio of $\bar{p}_{\text{T/S}}$ (high field)/ $\bar{p}_{\text{T/S}}$ (zero field) at early times comes into play, which approaches a value of 1/3 (cf. fig. 3b). With our estimated $k_{\text{diff,mic}}$ of $2 \times 10^8 \text{ s}^{-1}$ we are in fact in this region which is in fair accordance with our maximum magnetic-field effect of a factor 2.7 (cf. n_{rec} in fig. 2).

The arguments given here are based on the curves $\bar{p}_{\text{T/S}}$ which are valid only for triplet radical pairs with a random distribution of nuclear spin states. Since $\bar{p}_{\text{T/S}}(t \leq \tau_{\text{diff,mic}})$ is rather small it is clear that many encounters have to take place until the greater fraction of the radical pairs have recombined within the geminate phase in the same micelle. After the first reactions have taken place the nuclear spin population is more and more deprived of spin states producing efficient T/S transitions. Thus the $\bar{p}_{\text{T/S}}(t)$ curves which would be obtained after several encounters show increasingly slower ISC. On the other hand, this effect has to be taken into account quantitatively in order to describe adequately the kinetics if geminate recombination is more efficient than escape. Such calculations are quite involved and will not be reported here. Nevertheless from our present qualitative discussion two important conclusions may be drawn:

- (i) The effective rate constant of recombination does not only provide information on the spin motion but also on the *diffusion dynamics* of the radical pair.
- (ii) Besides the magnitude of the hfc constants involved, the magnitude of $k_{\text{diff,mic}}$ must be considered, to understand the characteristic field dependence of the radical-pair recombination rate. This is illustrated by fig. 3b. Since only time intervals of the order of $1/k_{\text{diff,mic}}$ are available for spin development it follows from this diagram that the larger $k_{\text{diff,mic}}$ the higher the magnetic field necessary to influence the spin motion during the available time interval. This is analogous to the lifetime uncertainty broadening effect reported recently as a function of the observation time of the geminate radical pairs [26,27].

The results of the quantitative treatment will have to show if the combined consideration of spin motion and diffusion are sufficient for a quantitative explanation and exploitation of our observations or if other interactions (particularly exchange interaction) must be taken into account. Furthermore, experiments are

in progress in order to determine the rate constants k_{rec} and k_{esc} by time-resolved measurements on the ns time scale.

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